

1058,188



PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Method for preparing Highly Siliceous Zeolite-Type Materials and Materials resulting therefrom

ERRATA

SPECIFICATION No. 1,058,188

Page 6, line 24, for "employed" read "employed"

Page 8, line 40, for "dichiardite" read "dachiardite"

Page 8, line 44, for "No. 77,233" read "No. 777,233"

Page 8, line 71, for " $1.0 \pm 0.1 \text{ M}_2\text{O}$:" read " $1.0 \pm 0.1 \text{ M}_2\text{O}$:"Page 10, line 32, for "NaO" read " Na_2O "

Page 10, line 69, for "crystallization" read "recrystallization"

Page 11, line 2, for "has" read "have"

Page 11, line 41, for "material" read "materials"

Page 11, line 56, for "structure" read "structures"

Page 14, line 39, for "effecting" read "affecting"

Page 20, line 11, for " AlO_3 " read " Al_2O_3 "

Page 20, line 87, for "steam" read "steamed"

Page 26, line 45, for " NH_2OH " read " NH_4OH "THE PATENT OFFICE
24th July 1967

35 in a variety of ways to take advantage of these properties.

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Method for preparing Highly Siliceous Zeolite-Type Materials and Materials resulting therefrom

We, MOBIL OIL CORPORATION, formerly Socony Mobil Oil Company, Inc., a corporation organized and existing under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York 17, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of preparing highly siliceous crystalline zeolite-type materials and materials resulting therefrom and, more particularly, to a novel technique for increasing the silica to alumina ratio of zeolites and to the zeolites or zeolite-type materials resulting therefrom.

Zeolite materials, both natural and synthetic, have been demonstrated in the past to have catalytic capabilities for various types of hydrocarbon conversion. Certain zeolite materials are ordered crystalline aluminosilicates having a definite crystalline structure within which there are a large number of small cavities which are interconnected by a number of still smaller channels. These cavities and channels are precisely uniform in size. Since the dimensions of these pores are such as to accept for adsorption molecules of certain dimensions while rejecting those of larger dimensions, these materials have come to be known as "molecular sieves" and are utilized in a variety of ways to take advantage of these properties.

Such molecular sieves include a wide variety of positive ion-containing crystalline aluminosilicates, both natural and synthetic. These aluminosilicates can be described as a rigid three-dimensional network of SiO_4 and AlO_4 tetrahedra in which the tetrahedra are cross-linked by the sharing of oxygen atoms whereby the ratio of the total aluminum and silicon

atoms to oxygen atoms is 1:2. The electrovalence of the tetrahedra containing aluminum is balanced by the inclusion in the crystal of a cation, for example, an alkali metal or an alkaline earth metal cation. This equilibrium can be expressed by formula wherein the ratio of Al_2 to the number of the various cations, such as Ca, Sr, Na_2 , K_2 or Li_2 , is equal to unity. One cation may be exchanged either in entirety or partially by another cation utilizing ion exchange techniques as discussed hereinbelow. By means of such cation exchange, it is possible to vary the size of the pores in the given aluminosilicate by suitable selection of the particular cation. The spaces between the tetrahedra are occupied by molecules of water prior to dehydration. The parent zeolite is dehydrated to activate it for use as a catalyst.

The stability of the exchanged crystalline aluminosilicates in the presence of heat, steam and acid, as well as their catalytic properties in general, are to a great extent dependent upon the silica-alumina ratio in the crystal lattice of the aluminosilicate. Generally speaking, the higher the silica-alumina ratio in the aluminosilicate, the greater the stability to heat, steam and acid.

In synthetic aluminosilicates, the silica/alumina ratio is essentially determined by the specific materials and the relative quantities of such materials used in the preparation of the zeolite. Naturally occurring zeolites are available, of course, with a fixed silica-alumina ratio. Up to the present time, no truly effective technique was known to alter drastically the silica-alumina ratio in natural crystalline aluminosilicates or in synthetic crystalline aluminosilicates after the latter have been formed. Since in many respects it would be advantageous to be able to convert an existing crystalline aluminosilicate to a crystalline material having a greater silica-alumina ratio, the desirability of a process which would make

such conversion feasible from an economical and chemical standpoint would, quite obviously, be greatly desirable.

In accordance with the present invention, it has now been found, for the first time, that it is possible to change drastically the silica-alumina ratio in crystalline aluminosilicates, modify their crystalline character to result in a shift to shorter metal-oxygen interatomic distances (measured as lattice cell constant, a_0) yet, at the same time, to obtain an improved zeolite or zeolite-like material having one or more enhanced catalytic properties. In accordance with the present invention, it is also possible to accomplish the same results with isomorphs of crystalline aluminosilicates.

It is accordingly a primary object of the present invention to provide a novel and effective process for increasing the silica-alumina ratio of crystalline aluminosilicates.

It is another important object of the present invention to provide a novel and effective process for the selective removal of aluminum from crystalline aluminosilicates by means of a hydrolysis technique.

It is a further object of the present invention to provide a novel and effective process for the selective removal of aluminum from crystalline aluminosilicates by means of a combined hydrolysis-chelation technique.

It is a further object of the present invention to provide a process for the selective removal of aluminum by means of molecules or ions which can complex strongly with trivalent aluminum to form aluminum complexes which may be removed from the aluminum-deficient aluminosilicate.

It is still another important object of the present invention to provide a novel process for obtaining a significant increase in the silica-alumina ratio of crystalline aluminosilicates, which process is capable of improving the stability of such aluminosilicates to heat, steam and acid without excessive loss in crystallinity, while providing aluminosilicates with improved catalytic properties including in many cases an increase in sorptive capacity.

It is another object of the present invention to provide a process capable of increasing the silica-alumina ratio in crystalline aluminosilicates up to 50/1 or higher by means of a novel chelation technique, said novel technique permitting the use of starting materials having a silica-alumina ratio lower than 6/1 and even as low as 2/1.

These important objects and advantages of the present invention will become more apparent upon reference to the ensuing description and appended claims.

According to the present invention there is

provided a process of increasing the silica/alumina ratio in the crystal lattice of a crystalline zeolite aluminosilicate which comprises exposing the aluminosilicate, while at least partially in the hydrogen form, to hydrolysis to such extent that at least 50% of the crystallinity of the aluminosilicate is retained, and treating the aluminosilicate to remove at least part of the aluminum thus displaced from the crystal lattice.

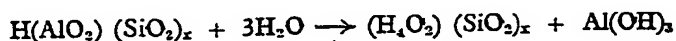
In order to remove aluminum effectively from the crystalline aluminosilicate, it is essential that the aluminum first be displaced from the tetrahedral sites in the anionic crystal lattice of the aluminosilicate. In accordance with the present invention, this step is effected through the formation of a zeolite at least partially in the hydrogen (or acid) form and the subsequent hydrolysis of the acid zeolite. More specifically, a portion of the cation of the zeolite must at some point be hydrogen. It is the hydrolysis of those aluminum sites associated with such hydrogen ions which causes the zeolite to lose aluminum from the zeolite framework.

The accompanying Drawing illustrates graphically how the silica/alumina ratio in crystalline zeolite aluminosilicates may be increased, with at least 50% of crystal retention, by removal of alumina by hydrolysis. The acceptable area of alumina removal is defined by lines A and B which show the maximum and minimum amounts of acceptable alumina removal respectively.

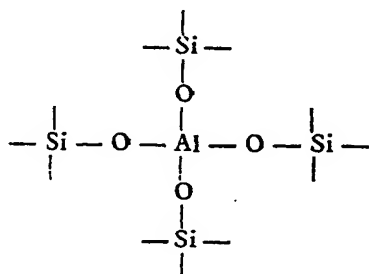
Having displaced aluminum from the tetrahedral sites of the aluminosilicate, this aluminum is separated from the aluminosilicate. In accordance with the present invention, this is accomplished by means of a suitable complexing agent to complex the aluminum into a form which facilitates its separation from the aluminosilicate.

The several aspects of the present invention will best be understood by first broadly postulating the theory which it is understood is involved in the practice of the present invention and then following such postulated theory with a discussion setting forth specific applications of such theory.

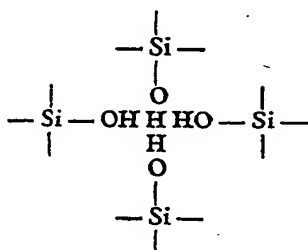
Following the formation of the hydrogen or acid form of the zeolite (the specific methods of effecting which will be discussed hereinafter), the aluminum is displaced from the tetrahedral sites in the aluminosilicate. While the present invention is not so limited, this removal is effectively illustrated by reference to the use of a hydrolysis technique for such purpose. Upon the reaction of the acid zeolite with water, the hydrolysis is postulated as proceeding as follows:



In the above equation, (H_4O_4) represents the tetrahedral structure of the zeolite which experimental data indicates is formed following the hydrolysis. The initial tetrahedral structure (before hydrolysis) may be represented as follows:



During hydrolysis, it is postulated that the aluminum ion in the tetrahedra is replaced by four protons, as follows:



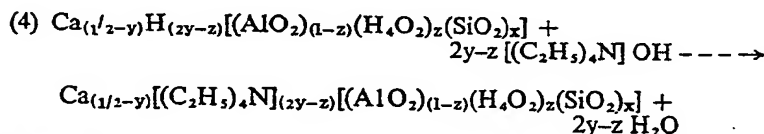
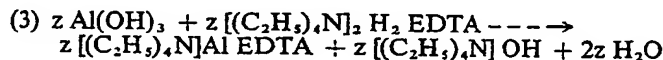
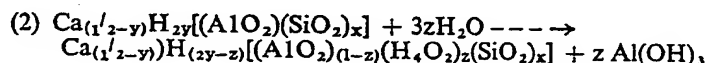
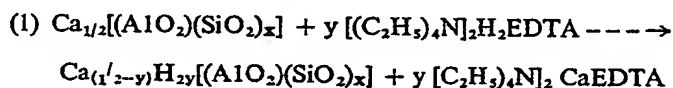
Thus, the (H_4O_4) represents the four protons contained in the oxygen tetrahedron set forth above. These formulae will be alluded to at a later point in this specification since this structure is extremely pertinent to an essential aspect of the present invention.

As previously indicated, while the hydrolysis reaction suffices to remove aluminum from the

tetrahedral sites of the aluminosilicate (the degree of hydrolysis depending upon the amount of aluminum removal desired), it is still necessary to separate this aluminum from the aluminosilicate. In accordance with the present invention, an extremely effective technique for such separation involves the use of complexing, preferably chelating, agents to form aluminum complexes which are readily separable from the aluminosilicate proper.

An extremely effective method of removing aluminum from the aluminosilicate with a minimum of effort and procedural steps involves the use of complexing agents which are effective not only to separate the aluminum physically from the aluminosilicate but to convert the aluminosilicate to its hydrogen or acid form prior to such separation, thus obviating the requirement for a preliminary acidification step. This procedure which forms a preferred aspect of the present invention, may best be explained in terms of the various reactions which take place when such a complexing agent is employed. For purposes of simplification of such explanation, the series of equations in question will be set forth in terms of a calcium form of aluminosilicate and a quaternary ammonium chelating agent. The specific quaternary ammonium chelating agent will be represented by the compound di(tetraethylammonium) dihydrogen ethylenediaminetetraacetate. [NOTE: When used in this specification, "EDTA" will represent ethylenediaminetetraacetic acid; when "EDTA" is set forth as part of a larger compound, viz., as the "EDTA" radical, it will represent the ethylenediaminetetraacetate radical.]

Having defined the reactants, the following equations apparently satisfactorily illustrate the use of a complexing agent not only to separate the aluminum physically from the aluminosilicate but to acidify such aluminosilicate prior to such physical separation:



In the above equations, $x > 2.0$; y represents moles of Ca^{++} removed from the zeolite; and

z represents moles of AlO_2 — removed from the zeolite.

As will be seen from the above series of equations, the foregoing process takes place in a series of four stages. In the first stage, the zeolite undergoes attack by the hydrogen ions of the chelating agent with such hydrogen ions being substituted for at least a portion of the cations of the zeolite. In the second stage, the acid zeolite formed in the first stage hydrolyzes to form a compound deficient in alumina. At this point in the process, the aluminum which has been removed from the tetrahedral sites of the aluminosilicate is still physically present on the aluminosilicate. In the third stage of the process, the aluminum hydroxide formed in the second stage reacts with excess of the chelating agent to form a quaternary ammonium hydroxide and an aluminum chelate. Finally, in the fourth and last stage of the process, the quaternary ammonium hydroxide reacts with the hydrolyzed acid zeolite formed in the second stage of the process to form the quaternary ammonium form of the alumina-deficient zeolite.

In view of the significant advantages of the procedure described immediately above in using a complexing agent which not only effects physical removal of the aluminum from the aluminosilicate but effects the initial acidification of the aluminosilicate, it is obviously desirable to use such technique whenever possible. While such technique may be effectively carried out with a number of specific aluminosilicates utilizing a large variety of complexing agents (as shown, merely by way of illustration, in Examples 1—20), however, there are situations in which, for one reason or another, it is not possible to follow this simplified procedure. For example, when a disodium dihydrogen EDTA chelating agent is used to treat a sodium zeolite Y aluminosilicate for purposes of removing alumina, without preliminary acidification of the zeolite, it will be found that no significant quantity of alumina is removed. The reason for this is that disodium dihydrogen EDTA is exceedingly weak as an acid and does not provide enough acidity to convert the sodium zeolite Y into its acid form. Since, as indicated previously, it is necessary that the zeolite be in its acid form so as to undergo hydrolysis before the complexing agent will be effective to remove aluminum physically from the aluminosilicate, it will be apparent that the silica:alumina ratio of the aluminosilicate may not be increased by the above technique utilizing the zeolite and chelating agent in question.

On the other hand, where disodium dihydrogen EDTA is used to remove alumina from calcium zeolite Y without the preliminary acidification of the zeolite, the treatment is fairly effective in removing alumina without any loss in sorptive capacity (see Example 1). The reason for the effectiveness of the disodium dihydrogen EDTA in this case is that the com-

plex which is formed by the calcium ion and the chelating agent is so stable that the disodium dihydrogen EDTA is willing to sacrifice its two weak hydrogens to pick up the calcium ion, this great stability of the calcium complex providing the potential to cause the reaction to proceed as it does. Thus, where calcium zeolite Y is concerned, a chelating agent such as disodium dihydrogen EDTA may be effectively utilized for the purpose of removing alumina from the zeolite.

But notwithstanding the inability of the disodium hydrogen EDTA to remove alumina from a compound such as sodium zeolite Y without preliminary acidification of the zeolite, the process of the present invention is nevertheless applicable to such a system to effect the removal of the alumina from the zeolite. More specifically, all that need be done in such case is to pretreat the zeolite to convert it at least partially to its acid or hydrogen form and to hydrolyse such acid zeolite, followed by subsequent treatment with a complexing agent (which may be disodium dihydrogen EDTA) to separate the aluminum physically from the aluminosilicate. Such a procedure is clearly illustrated in Example 44. In this technique, however, it is important to note that the complexing agent in such case is used simply to chelate or complex the aluminum but is not relied upon in any way to provide the acid zeolite which is necessary before such chelation takes place.

In those instances in which the complexing agent is to be used not only to effect physical removal of the alumina but to effect the initial acidification of the aluminosilicate, it is necessary, as will be appreciated from the foregoing discussion, to use a hydrogen ion-containing complexing agent whose hydrogen ions will exchange into the particular aluminosilicate being treated. In general, it may be stated that most effective results are obtained when a complexing agent is employed which will bring the pH of the reaction mixture below 7 and preferably 6 at least at some point during the reaction. This desideratum may be obtained most effectively when the pH of the complexing agent employed is no greater than 6. By using complexing agents of at least this degree of acidity, the reaction potential will ordinarily be sufficiently great to cause the hydrogen ions of such agent to exchange into the aluminosilicate.

On the other hand, it should be noted that one of the significant advantages of using complexing agents which not only are effective to remove the aluminum from the solvolyzed aluminosilicate but to convert the aluminosilicate to its acid form is that such complexing agents permit highly controlled rates of formation of the hydrogen or acid zeolite and, at the same time, a controlled rate of hydrolysis of said acid zeolite. Consistent with this significant advantage, it is important to con-

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sider that negative results can be obtained if the pH of the complexing agent is too low, in which case the high degree of control provided by such complexing agent may be lost.

5 Even here, however, the acidity which the aluminosilicate can tolerate will depend to a great degree upon the silica/alumina ratio of the starting material. With high silica/alumina ratios such as exist in mordenite, high acidity

10 can be tolerated. On the other hand, where lower silica-alumina ratios are involved, such as exist in synthetic faujasite, more care must be taken to avoid uncontrolled acid attack on the zeolite and, accordingly, higher pH's are

15 preferred in such case. The merit of the process of the present invention is, of course, that where complexing agents are used which not only physically remove the alumina from the solvolyzed aluminosilicate but serve to acidify

20 the aluminosilicate in the first instance, the high degree of control provided permits the treatment of aluminosilicates which have silica-alumina starting ratios lower than 6/1 and even at low as 2/1 without danger of destruction

25 of the aluminosilicate crystal lattice, though most effective results are obtained using aluminosilicates which have initial silica-alumina ratios of 4 to 1 or more.

In those instances where, due to the specific

30 nature of the aluminosilicate and the complexing agent (as described above) it is not possible to effect the acidification of the aluminosilicate during the course of the complexing procedure, the aluminosilicate may be pre-

35 treated to put it in acid form to the desired degree of acidification. To accomplish such acidification, the aluminosilicate may be contacted with a non-aqueous or aqueous fluid medium comprising a gas, polar solvent or

40 water solution containing the desired ions, such ions being introduced by means either of a hydrogen ion-containing fluid medium or a fluid medium containing ammonium ions capable of conversion to hydrogen ions (the latter

45 procedure having been used in the process of Example 44).

Water is the preferred medium for reason of economy and ease of preparation in large scale operations involving continuous or batch-

50 wise treatment. Similarly, for this reason, organic solvents are less preferred but can be employed providing the solvent permits ionization of the acid or the ammonium compound. Typical solvents include cyclic and acyclic

55 ethers such as dioxane, tetrahydrofuran, ethyl ether, diethyl ether and diisopropyl ether; ketones such as acetone and methyl ethyl ketone; esters such as ethyl acetate, propyl acetate; alcohols such as ethanol, propanol and

60 butanol; and miscellaneous solvents such as dimethylformamide.

The hydrogen ion or ammonium ion may be present in the fluid medium in an amount varying within wide limits dependent upon the

65 pH value of the fluid medium. Where the

aluminosilicate material has a molar ratio of silica to alumina greater than 5.0, the fluid medium may contain a hydrogen or ammonium ion equivalent to a pH value ranging from less than 1.0 up to a pH value of 10.0. Within

70 these limits, pH values for fluid media containing an ammonium ion range from 4.0 to 10.0 and are preferably between a pH value of 4.5 to 8.5. For fluid media containing a

75 hydrogen ion alone, the pH values range from less than 1.0 up to 7.0 and are preferably within the range of less than 3.0 up to 6.0. Where the molar ratio of the aluminosilicate is greater than 3.0 and less than 5.0, the pH

80 value for the fluid media containing a hydrogen ion ranges from 3.8 to 8.5. Where ammonium ions are employed, the pH value ranges from 4.5 to 9.5 and is preferably within the limit of 4.5 to 8.5. When the aluminosilicate

85 material has a molar ratio of silica to alumina less than 3.0, the preferred medium is a fluid containing an ammonium ion instead of a hydrogen ion. Thus, depending upon the silica to alumina ratio, the pH value varies within

90 rather wide limits.

In carrying out the treatment with the fluid medium, the procedure employed comprises contacting the aluminosilicate with the desired

95 fluid medium or media until such time as metallic cations originally present in the aluminosilicate are removed to the desired extent. Repeated use of fresh solution of the

entering ion is of value to secure more complete exchange. The degree of exchange will, of course, depend on the amount of aluminum

100 one wants to remove, the greater the degree of acidification of the aluminosilicate the greater the aluminum removal as a general rule.

Elevated temperatures tend to hasten the

105 speed of treatment whereas the duration thereof varies inversely with the concentration of the ions in the fluid medium. In general, the temperatures employed range from below

110 ambient room temperature of 24°C. up to temperatures below the decomposition temperature of the aluminosilicate. Following the fluid treatment, the treated aluminosilicate is washed with water, preferably

115 distilled water, until the effluent wash water has a pH value of approximately that of the inlet wash water, i.e., between about 5 and 8. The aluminosilicate material is thereafter analyzed for metallic ion content by

120 methods well known in the art. Analysis also involves analyzing the effluent wash for anions obtained in the wash as a result of the treatment, as well as determination of and correction for anions that pass into the effluent wash

125 from soluble substances or decomposition products of insoluble substances which are otherwise present in the aluminosilicate as impurities.

The actual procedure employed for carrying out the fluid treatment of the aluminosilicate

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may be accomplished in a batchwise or continuous method under atmospheric, subatmospheric or superatmospheric pressure. A solution of the ions of positive valence in the form of a molten material, vapor, aqueous or non-aqueous solution, may be passed slowly through a fixed bed of the aluminosilicate. If desired, hydrothermal treatment or a corresponding non-aqueous treatment with polar solvents may be effected by introducing the aluminosilicate and fluid medium into a closed vessel maintained under autogeneous pressure. Similarly, treatments involving fusion or vapor phase contact may be employed providing the melting point or vaporization temperature of the acid or ammonium compound is below the decomposition temperature of the aluminosilicate.

A wide variety of acidic compounds can be employed with facility as a source of hydrogen ions and include both inorganic and organic acids.

Representative inorganic acids which can be employed include acids such as hydrochloric acid, hypochlorous acid, chloroplatinic acid, sulfuric acid, sulfurous acid, hydrosulfuric acid, peroxydisulfonic acid ($\text{H}_2\text{S}_2\text{O}_8$), peroxymonosulfuric acid (H_2SO_5), dithionic acid ($\text{H}_2\text{S}_2\text{O}_6$), sulfamic acid ($\text{H}_2\text{NHS}_3\text{H}$), amidodisulfonic acid [$\text{NH}(\text{SO}_3\text{H})_2$], chlorosulfuric acid, thiocyanic acid, hyposulfurous acid ($\text{H}_2\text{S}_2\text{O}_4$), pyrosulfuric acid ($\text{H}_2\text{S}_2\text{O}_7$), thiosulfuric acid ($\text{H}_2\text{S}_2\text{O}_3$), nitrosulfonic acid (HSO_3NO), hydroxylamine disulfonic acid [$(\text{HSO}_3)_2\text{NOH}$], nitric acid, nitrous acid, hyponitrous acid and carbonic acid.

Typical organic acids which find utility in the practice of the invention include the monocarboxylic, dicarboxylic and polycarboxylic acids which can be aliphatic, aromatic or cycloaliphatic in nature.

Representative aliphatic monocarboxylic, dicarboxylic and polycarboxylic acids include the saturated and unsaturated, substituted and unsubstituted acids such as formic acid, acetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromoacetic acid, propionic acid, 2-bromopropionic acid, 3-bromopropionic acid, lactic acid, n-butyric acid, isobutyric acid, crotonic acid, n-valeric acid, isovaleric acid, n-caproic acid, oenanthic acid, pelargonic acid, capric acid, undecyclic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, alkylsuccinic acid, alkenylsuccinic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid, glutonic acid, muconic acid, ethylidene malonic acid, isopropylidene malonic acid and allyl malonic acid.

Representative aromatic and cycloaliphatic monocarboxylic, dicarboxylic and polycarboxylic acids include 1,2-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid,

2-carboxy-2-methylcyclohexaneacetic acid, phthalic acid, isophthalic acid, terephthalic acid, 1,8-naphthalenedicarboxylic acid, 1,2-naphthalenedicarboxylic acid, tetrahydrophthalic acid, 3-carboxycinnamic acid, hydrocinnamic acid, pyrogalllic acid, benzoic acid, ortho, meta and para-methyl, hydroxy, chloro, bromo and nitro-substituted benzoic acids, phenylacetic acid, mandelic acid, benzylic acid, hippuric acid, benzenesulfonic acid, toluenesulfonic acid and methanesulfonic acid.

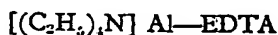
Other sources of hydrogen ions include carboxy polyesters prepared by the reaction of an excess of polycarboxylic acid or an anhydride thereof and a polyhydric alcohol to provide pendant carboxyl groups.

Still other materials capable of providing hydrogen ions are ion exchange resins having exchangeable hydrogen ions attached to base resins comprising cross-linked resinous polymers of monovinyl aromatic monomers and polyvinyl compounds. These resins are well known materials which are generally prepared by copolymerizing in the presence of a polymerization catalyst one or more monovinyl aromatic compounds, such as styrene, vinyl toluene, vinyl xylene, with one or more divinyl aromatic compounds such as divinyl benzene, divinyl toluene, divinyl xylene, divinyl naphthalene and divinyl acetylene. Following copolymerization, the resins are further treated with suitable acids to provide the hydrogen form of the resin.

Still another class of compounds which can be employed are ammonium compounds which decompose to provide hydrogen ions when an aluminosilicate treated with a solution of said ammonium compound is subjected to temperatures below the decomposition temperature of the aluminosilicate.

Representative ammonium compounds which can be employed include ammonium chloride, ammonium bromide, ammonium iodide, ammonium carbonate, ammonium bicarbonate, ammonium sulfate, ammonium sulfide, ammonium thiocyanate, ammonium dithiocarbamate, ammonium peroxysulfate, ammonium acetate, ammonium tungstate, ammonium molybdate, ammonium benzoate, ammonium borate, ammonium carbamate, ammonium sesquicarbonate, ammonium chlorophosphate, ammonium citrate, ammonium dithionate, ammonium fluoride, ammonium gallate, ammonium nitrate, ammonium nitrite, ammonium formate, ammonium propionate, ammonium butyrate, ammonium valerate, ammonium lactate, ammonium malonate, ammonium oxalate, ammonium palmitate and ammonium tartrate. Still other ammonium compounds which can be employed include complex ammonium compounds such as tetramethylammonium hydroxide, trimethylammonium chloride. Other compounds which can be employed are nitrogen bases such as the salts of guanidine, pyridine and quinoline.

An essential feature of the present invention is that by a judicious choice of the complexing agent which is used to remove the aluminum physically from the aluminosilicate following the hydrolysis reaction, such removal may be greatly facilitated. More specifically, if a complexing agent is selected which forms a soluble complex or chelate with the metal cations which are removed from the aluminosilicate, the physical separation of the aluminum from the aluminosilicate will simply involve the removal (by filtration) of the resulting solution from the solid aluminosilicate. Restating the foregoing in terms of the four-stage process previously discussed, if the complex



is soluble in aqueous solution, separation problems will have been virtually eliminated since the chelated aluminosilicate is insoluble in water. Specific examples of such a procedure include (merely by way of illustration) Examples 1—20, in each of which a complex chelate is formed which is water soluble.

It is to be understood, however, that the above solubility characteristic, whilst preferred, is not essential. More specifically, as will be shown in Example 45, it is possible to remove the aluminum physically from the aluminosilicate without dissolving it by use of a chelating resin which may be physically separated from the aluminosilicate product by means of a conventional screening process, since the resin beads are relatively large compared to the chelated zeolite, which has dimensions in the order of microns. It will be noted from Example 45, however, that notwithstanding the fact that the aluminum removed from the aluminosilicate is not solubilized, the chelating resin is nevertheless usable to form the acid zeolite as a preliminary to the aluminum removal, at least in the case of the calcium zeolite Y which was used in said example. Thus, the significant advantages of the present invention are retained notwithstanding the different technique of removal of the aluminum from the aluminosilicate.

As will be apparent, a variety of complexing agents may be used to remove the aluminum from the hydrolysed zeolite in accordance with the present invention, the essential requirement being that such agents must form coordination complexes with aluminum. The preferred complexing agents are those which form stable chelates with aluminum. In the case of a complexing agent which is intended to form soluble complexes or chelates for ease of removal of the aluminum from the aluminosilicate, the complexing agent should form a stable complex or chelate with aluminum which is soluble in the medium in which the complexing is carried out. When the complexing agent is to be used to acidify the aluminosilicate

prior to complexing, the complexing agent should also exist initially either in its acid form or as an acid salt, should form a stable complex or chelate with at least one cation present in the zeolite to be treated and should have a pH in solution no greater than 7 and preferably no greater than 6. In all cases, the complexing agent should be so selected that complexing takes place slowly enough to avoid destruction of the crystalline, aluminum-deficient, zeolite product.

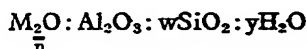
In those cases where the complexing agent is also to be used to convert the aluminosilicate to its hydrogen or acid form, the complexing agent should be so selected that the non hydrogen cation of the complexing agent is sufficiently large so that it will not exchange into the aluminosilicate. By means of such size selection, the non-hydrogen cations of the complexing agent will not compete for the available cation sites in the aluminosilicate with the hydrogen ions and prevent effective acidification of the aluminosilicate, which acidification must take place for the effective alumina removal of the present invention. Extremely effective complexing agents for this purpose are those containing tetraethylammonium cations such as those previously mentioned.

Examples of complexing agents which are extremely effective in carrying out the process of the present invention include (but are not restricted to) di(tetraethylammonium) dihydrogen EDTA; EDTA (ethylenediaminetetraacetic acid); diammonium dihydrogen EDTA; ammonium acid manganese EDTA; fluorides, such as sodium or ammonium fluoride; carboxylic and polycarboxylic acids and acid salts, such as citric acid and ammonium acid citrate; mixtures of such complexing agents, etc. An example of the type of complexing agent which does not form a soluble complex is, as previously stated, an anion exchange resin in the dihydrogen ethylenediaminetetraacetate form.

Various other complexing agents, containing a variety of anionic portions, may also be used in the process of the present invention provided they meet the criteria set forth hereinbefore. For a comprehensive review of complexing agents, see "Organic Sequestering Agents" by Stanley Chaberek and Arthur E. Martell, published by John Wiley and Sons, Inc., New York (1959), and an article entitled ("Chelation" by Harold F. Walton, Scientific American, June 1953, pp. 68—76, both of which are hereby incorporated by reference.

In general, complexing should preferably take place at temperatures of about 20—100°C. for periods of at least 2 hours. Extended periods of reaction are normally not detrimental and, in some cases, could be desirable.

The zeolites which may be treated in accordance with the present invention may, in their hydrated form, be represented by the following formula



wherein M is a cation which balances the electrovalence of the tetrahedra, n represents the valence of the cation, w the moles of SiO₂ and y the moles of H₂O, the removal of which produces the characteristic open network system of the molecular sieves.

Cation M should preferably form a stable chelate with the chelating agent to be used in the process of the present invention. For example, excellent results have been obtained in light of the foregoing requirement wherein cation M is calcium or one of the rare earth metals. Excellent results have also been obtained with other cations, e.g., sodium.

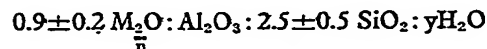
As indicated previously, the SiO₂:Al₂O₃ ratio (viz., the value of w) should be at least 2:1 initially, and preferably at least 4:1. Indeed, particularly excellent results are obtained with ratios above 4:1 and less than 6:1. As a result of the present process, zeolites or zeolite-like products may be obtained having a silica-alumina ratio as high as 50/1, if not higher.

The particular zeolite which is utilized in the process of the present invention should be capable of accommodating at least one cation (viz., "M") which forms a stable complex or chelate with the complexing agent utilized in the process and should also be capable of undergoing limited attack by hydrogen ions which results in the loss of at least a portion of its alumina. Particularly advantageous zeolites meeting these qualifications (although this list

is not intended to be exhaustive) include zeolites of the following groups: X; B; D; L; Q; R; S; T; Y; Z; ZK-4; ZK-5; and natural zeolite materials such as faujasite; heulandite; clinoptilolite; chabazite; gmelinite; mordenite; and dichardite.

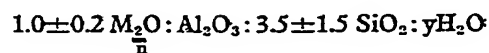
Following is a description of exemplary zeolites usable in the process of the present invention:

Zeolite X (U.K. Specification No. 77,233) is a synthesized crystalline aluminosilicate which can be represented in terms of mole ratios of oxides as follows:



wherein M is a cation as hereinbefore defined, n represents the valence of M, and y is a value up to eight depending on the identity of M and degree of hydration of the crystal:

The formula for Zeolite B (U.K. Specification Nos. 777,233 and 898,457) may be written in terms of oxide mole ratios as:



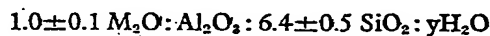
wherein M represents a cation as hereinbefore defined, n is the valence of the cation, and y has an average value of 5.1 but may range from 0 to 6.

The formula for Zeolite D (U.K. Specification No. 868,846), in terms of oxide mole ratios, may be represented as:



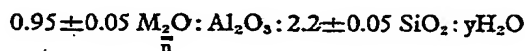
wherein x is a value of 0 to 1, w is from 4.5 to about 4.9 and y, in the fully hydrated form, is about 7.

The composition of Zeolite L (U.K. Specification No. 909,264), in oxide mole ratios, may be represented as



wherein M designates a cation as hereinbefore defined, n represents the valence of M and y is any value from 0 to 7.

The formula for Zeolite Q (U.K. Specification No. 897,670), expressed in terms of oxide mole ratios, may be written as:



wherein M is a cation as hereinbefore defined, n is the valence of the cation, and y is any value from 0 to 5.

The formula for Zeolite R (U.K. Specification No. 841,812) in terms of oxide mole ratios may be written as follows:

wherein w is from 2.45 to 3.65, and y, in the hydrated form, is about 7.

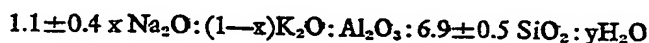
The formula for Zeolite S (U.K. Specification No. 909,265) in terms of oxide mole ratios may be written as:



wherein w is from 4.6 to 5.9 and y, in the hydrated form, is about 6 to 7.

The formula for Zeolite T (U.K. Specifi-

cation No. 912,936) in terms of oxide mole ratios may be written as:



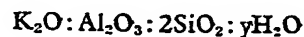
wherein x is any value from about 0.1 to about 0.8 and y is any value from about 0 to about 8.

The formula for Zeolite Y (U.K. Specification No. 909,266) expressed in oxide mole ratios is:



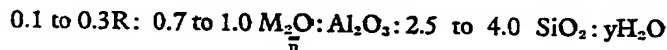
wherein w is a value ranging from 3 to 5 and y may be any value up to about 9.

The formula for Zeolite Z (U.K. Specification No. 828,936) in terms of oxide mole ratios may be written as:



wherein y is any value not exceeding 3.

Zeolite ZK—4 can be represented in terms of mole ratios of oxides as:



wherein R is a member selected from the group consisting of methyl-ammonium oxide, water and mixtures thereof with one another, M is a cation as hereinbefore defined, n is the valence of the cation, and y is any value from about 3.5 to about 5.5.

Zeolite ZK—4 can be prepared by preparing an aqueous solution of oxides containing Na_2O , Al_2O_3 , SiO_2 , H_2O and tetramethyl-ammonium ion having a composition, in terms of oxide mole ratios, which falls within the following ratios:

$\text{SiO}_2/\text{Al}_2\text{O}_3$	2.5 to 11
Na_2O	0.5 to 2.5
$\text{Na}_2\text{O} + [(\text{CH}_3)_4\text{N}]_2\text{O}$	
H_2O	25 to 30
$\text{Na}_2\text{O} + [(\text{CH}_3)_4\text{N}]_2\text{O}$	
$\text{Na}_2\text{O} + [(\text{CH}_3)_4\text{N}]_2\text{O}$	1 to 2
SiO_2	

maintaining the mixture at a temperature of 100°C. to 120°C. until the crystals are formed, and separating the crystals from the mother liquor. The crystal material is thereafter washed until the wash effluent has a pH essentially that of wash water and subsequently dried.

Zeolite ZK—5 is representative of another crystalline aluminosilicate which is prepared

in the same manner as Zeolite ZK—4 except that $\text{N}_2\text{N}'$ - dimethyltriethylenediammonium hydroxide is used in place of tetramethyl-ammonium hydroxide. Zeolite ZK—5 may be prepared from an aqueous sodium aluminosilicate mixture having the following composition expressed in terms of oxide mole ratios as:

$\text{SiO}_2/\text{Al}_2\text{O}_3$	2.5 to 11
Na_2O	0.5 to 2.5
$\text{Na}_2\text{O} + [(\text{CH}_2)_6\text{N}_2(\text{CH}_3)_2]\text{OH}$	
H_2O	25 to 50
$\text{Na}_2\text{O} + [(\text{CH}_2)_6\text{N}_2(\text{CH}_3)_2]\text{OH}$	
$\text{Na}_2\text{O} + [(\text{CH}_2)_6\text{N}_2(\text{CH}_3)_2]\text{OH}$	1 to 2
SiO_2	

The N,N' -dimethyltriethylenediammonium hydroxide used in preparing Zeolite ZK—5 can be prepared by methylating 1,4 - diazabicyclo - (2.2.2) - octane with methyl iodide or dimethyl sulfate, followed by conversion to the hydroxide by treatment with silver oxide or barium hydroxide.

In using the N,N' - dimethyltriethylene-diammonium hydroxide compound in the preparation of Zeolite ZK—5, the hydroxide may be employed per se, or further treated with a source of silica, such as silica gel, and thereafter reacted with aqueous sodium aluminate in a reaction mixture whose chemical composition corresponds to the above-noted oxide mole ratios. Upon heating at temperatures of 200 to 600°C., the methyl ammonium ion is converted to hydrogen ion.

Quite obviously, the above-listed molecular sieves are only representative of the synthetic crystalline zeolite molecular sieve catalysts which may be used in the process of the present invention, the particular enumeration of such sieves not being intended to be exclusive.

Molecular sieves are ordinarily prepared initially in the sodium form of the crystal. In general, the process of preparation involves heating, in aqueous solution, an appropriate mixture of oxides, or of materials whose chemical composition can be completely represented as a mixture of oxides NaO , Al_2O_3 , SiO_2 and H_2O at a temperature of approximately 100°C. for periods of 15 minutes to 90 hours or more. The product which crystallizes within this hot mixture is separated therefrom and water washed until the water in equilibrium with the zeolite has a pH in the range of 9 to 12. The substance is then ready for treatment in accordance with the process of the present invention to form the alumina-deficient zeolite, after which it may be activated for use by heating until dehydration is attained.

For example, in the preparation of sodium zeolite "X", suitable reagents for the source of silica include silica sol, silica gel, silicic acid or sodium silicate. Alumina can be supplied by utilizing activated alumina, gamma alumina, alpha alumina, aluminum trihydrate or sodium aluminate. Sodium hydroxide is suitably used as the source of the sodium ion and in addition contributes to the regulation of the pH. All reagents are preferably soluble in water. The reaction solution has a composition, expressed as mixtures of oxides, within the following ranges: SiO_2/Al_2O_3 of 3.0 to 5.0, Na_2O/SiO_2 of 1.2 to 1.5 and H_2O/Na_2O of 35 to 60. A convenient and generally employed process of preparation involves preparing an aqueous solution of sodium aluminate and sodium hydroxide and then adding with stirring an aqueous solution of sodium silicate.

The reaction mixture is placed in a suitable vessel which is closed to the atmosphere in

order to avoid losses of water and the reagents are then heated for an appropriate length of time. Adequate time must be used to allow for crystallization of the first amorphous precipitate that forms. While satisfactory crystallization may be obtained at temperatures from 21°C. to 150°C., the pressure being atmospheric or less, corresponding to the equilibrium of the vapor pressure with the mixture at the reaction temperature, crystallization is ordinarily carried out at about 100°C. As soon as the zeolite crystals are completely formed they retain their structure and it is not essential to maintain the temperature of the reaction any longer in order to obtain a maximum yield of crystals.

After formation, the crystalline zeolite is separated from the mother liquor, usually by filtration. The crystalline mass is then washed, preferably with salt-free water, while on the filter, until the wash water, in equilibrium with the zeolite, reaches a pH of 9 to 12. The crystals are then dried at a temperature between 25°C. and 150°C. The zeolite is then ready to be treated in accordance with the process of the present invention. After such treatment, activation may be attained through dehydration, as for example at 350°C. and 1 mm. pressure or at 350°C. in a stream of dry air.

In an earlier portion of the present specification, the respective tetrahedral structures of the aluminosilicate before and after hydrolysis were set forth and it was pointed out that, as a result of said hydrolysis, each of the affected aluminum ions in the tetrahedra was replaced by four protons or hydrogen atoms. This substitution is accompanied by an extremely interesting and significant physical phenomenon. More specifically, the oxygen to oxygen bond dimension in an AlO_4 tetrahedron is 2.90\AA and in a SiO_4 tetrahedron 2.64\AA . On the other hand, the ideal $O-H \cdots O$ distance, as observed in diaspore, can be taken as approximately 2.65\AA . Thus, the size of an H-bonded oxygen tetrahedron is therefore approximately equal to the size of a silica tetrahedron. Accordingly, by virtue of the substitution of four protons for a given aluminum atom during the hydrolysis reaction, the tetrahedron will be transformed to a structure which, by means of X-ray diffraction analysis, would appear to have been enriched in silica by virtue of the contraction of the bond distances.

In addition to indicating a slight contraction of the lattice structure in the treated aluminosilicate, X-ray diffraction analysis indicates a crystallographic structure (i.e., crystal symmetry) in the treated and untreated aluminosilicates which are substantially identical to one another. In view of this fact and since conventional elemental chemical analysis indicates an increase in the silicon-aluminum ratio as between the treated and untreated aluminosilicates

5 silicates, one would normally conclude that
aluminum atoms in the crystal structure has
been replaced by silicon atoms through a re-
crystallization technique. Since silicon and
aluminum atoms have essentially the same
atomic weight (about 28 and 27, respectively),
one would expect that the hydrocarbon adsorp-
tion capacity of the alumina-deficient treated
product per unit weight of such product would
be essentially the same as that of the un-
treated material, or one might possibly even
expect a decrease in such capacity due to the
slight contraction of the lattice structure of the
treated aluminosilicate as compared with the
untreated material.

Notwithstanding the foregoing, however, one
observes by means of standard hydrocarbon

adsorption tests that a substantial increase in
the hydrocarbon adsorption capacity per unit
weight of sample results from the treatment
of the aluminosilicate in accordance with the
present invention and further observes that this
capacity per unit weight of silica is substan-
tially the same in the treated and untreated
materials. This demonstrates that what was
indicated both by X-ray diffraction and
chemical analysis, viz., an absolute increase in
the quantity of silica per unit cell, is not the
case but that, on the contrary, aluminum atoms
have been removed from the tetrahedral sites
without their replacement by silicon atoms.
The following data, based upon adsorption
tests conducted to demonstrate the above,
support this conclusion:

Zeolite	Molar Ratio SiO ₂ /Al ₂ O ₃	g. Cyclohexane Sorbed/g. Sample	g. Cyclohexane Sorbed/g. SiO ₂ in Sample
Before Al removal	4.61	.191	.306
After Al removal	6.94	.231	.307
Before Al removal	4.45	.187	.296
After Al removal	8.30	.239	.303
Before Al removal	4.76	.196	.310
After Al removal	6.70	.227	.306

The observed increased cyclohexane sorptive
capacity of materials which have undergone
aluminum removal should serve to distinguish
between zeolites in which all tetrahedral sites
are occupied by silicon plus aluminum and
material which underwent loss of tetrahedral
aluminum from the zeolite.

As indicated above, aluminosilicates treated
in accordance with the present invention have
substantially the same crystal symmetry as the
untreated aluminosilicate. As a result, the treat-
ment of crystalline aluminosilicates in accor-
dance with the present invention can result in
aluminosilicates having a crystallographic
structure substantially the same as that of the
starting aluminosilicate but having different
silica-alumina ratios. For example, alumino-
silicates having the crystallographic structure
of faujasite can be prepared with silica-alumina

ratios in excess of 6/1. It is characteristic of
such faujasitic structure, as distinguished from
that of mordenite, that they possess channels
larger than 4Å° in at least two dimensions.
Similarly, aluminosilicates having the crystal-
lographic structure of chabazite but having a
silica/alumina ratio above 5/1 can be pre-
pared. Still further, porous crystalline alumino-
silicates having the crystallographic structure
of mordenite but having a silica-alumina ratio
above 10/1 can be prepared. As another
example, aluminosilicates having the crystal-
line structure of zeolite L can be prepared
by the process of the present invention with
silica-alumina ratios above 7/1.

Following are examples which will illus-
trate the various aspects and ramifications of
the present invention:

EXAMPLE 1:

This example demonstrates that disodium dihydrogen EDTA is fairly effective in removing alumina from calcium zeolite Y without any loss in sorptive capacity.

A solution was prepared by dissolving 6.4 g. of disodium dihydrogen EDTA dihydrate (17.2 millimoles) in 30 ml. of water. To the

solution was added 14.9 g. (8.24 g. on water-free basis) of calcium zeolite Y. This mixture was stirred and refluxed overnight. The solid product was collected on a Buchner funnel and washed with 50 ml. of water. A summary is given in Table A of the properties of the initial zeolite and the final product.

TABLE A

	Starting Material	Product
Wt. Percent		
Na ₂ O	2.3	7.5
CaO	10.6	2.66
Al ₂ O ₃	22.1	19.0
SiO ₂	64.9	69.0
Mole Percent		
Na ₂ O	2.44	8.04
CaO	12.40	3.16
Al ₂ O ₃	14.20	12.40
SiO ₂	71.0	76.40
Molar Ratio, SiO ₂ /Al ₂ O ₃	5.0	6.18
G. sorbed/100 g. Sample*		
Cyclohexane	19.6	20.5
Water	32.0	31.95

*[Note: The conditions under which the sorption of cyclohexane and water were determined both above and elsewhere in this specification were as follows: a weighed sample is contacted with the desired pure adsorbate vapor in an adsorption chamber at a pressure less than the vapor-liquid equilibrium pressure of the adsorbate at room temperature. This pressure is kept constant (20 mm. with cyclohexane; 12 mm. with water) during the adsorp-

tion period. Adsorption is complete when constant pressure is reached. The increase in weight is calculated as the adsorption capacity of the sample.]

An extremely effective method for removing alumina from zeolite Y consists in treating calcium zeolite Y with di (tetraethylammonium) dihydrogen EDTA. This method is illustrated in the following example:

EXAMPLE 2:

Sixty-six grams of EDTA were dissolved in 162 ml. of 3.25 N tetraethylammonium hydroxide. The resulting solution was diluted with 211 ml. of water. Fifty-five grams of calcium zeolite Y were added to the solution and the mixture was stirred and refluxed overnight. The highly dilatant solid product was

collected on a Buchner funnel and washed with several hundred milliliters of water. A portion of the air dried product was analyzed for Na_2O , CaO , Al_2O_3 , SiO_2 , C and N. A resume of the composition and properties of the starting material and the product are given in Table B:

TABLE B

Wt. Percent	Starting Material	Product
Na_2O	2.59	1.75
CaO	11.10	2.66
Al_2O_3	23.40 ignited	12.90 unignited
SiO_2	62.30 sample	52.6 sample
C	0	9.8
N	0	1.43
Mole Percent*		
Na_2O	2.75	2.61
CaO	13.00	4.40
Al_2O_3	15.10	11.70
SiO_2	69.1	81.1
*based on ignited sample		
Molar Ratio, $\text{SiO}_2/\text{Al}_2\text{O}_3$	4.61	6.94
G. Sorbed/100 G. Sample		
Cyclohexane	19.06	23.1
Water	31.5	35.1

The composition of the product obtained in Example 2 indicates that some other cation, in addition to sodium and calcium, is present.

More specifically, the following calculation shows that 40% of the cation sites are occupied by a cation other than sodium and calcium:

$$\frac{(\text{Mole } \% \text{ Al}_2\text{O}_3 - \text{Mole } \% \text{ Na}_2\text{O} - \text{Mole } \% \text{ CaO})}{\text{Mole } \% \text{ Al}_2\text{O}_3} \times 100 = \frac{(11.7 - 2.61 - 4.4)}{11.7} \times 100 = 40\%$$

The following calculation shows that 41% of the cation sites are occupied by a monovalent, nitrogen-containing cation:

$$\frac{\text{Wt. } \% \text{ N}}{28} \times \frac{102}{\text{Wt. } \% \text{ Al}_2\text{O}_3} \times 100 = \frac{1.43}{28} \times \frac{102}{12.9} \times 100 = 41\%$$

The next and last calculation shows that the monovalent, nitrogen-containing cation in the product is tetraethylammonium ion:

Wt. % C/Wt. % N

Found

6.8

Calc. for $(C_2H_5)_4N^+$

6.85

- 5 The next example shows that equation (1) [previously set forth above] does not go to completion but probably involves an equilibrium between EDTA and zeolite Y for calcium ion.

EXAMPLE 3:

In a manner similar to that described in Example 2, three samples of calcium zeolite Y were treated with various amounts of di (tetraethylammonium) dihydrogen EDTA solution. The results of these experiments are summarized in Table C: 10 15

TABLE C

Moles EDTA Used Per g-atom Ca in Ca Zeolite Y Used	Per cent Removed From Zeolite	
	Ca++	AlO ₂ ⁻
0.70	32	18
1.45	64	28
3.63	72	35

EXAMPLE 4:

A sample calcium zeolite Y was given four successive treatments with excess di (tetra-

ethylammonium) dihydrogen ethylenediamine-tetraacetate. Following is a summary of the properties of the zeolite after each treatment: 20

TABLE D

Treatment	Total % Removal Ca++	AlO ₂	Molar Ratio SiO ₂ /Al ₂ O ₃	g. Sorbed/100 g. Sample	
				Cyclohexane	Water
0	0	0	4.45	19.1	31.5
1	39	18	5.4	21.5	35.8
2	73	36	6.9	23.8	36.5
3	90	46	8.3	23.6	35.6
4	97	46	8.3	23.9	34.4

- 25 These data indicate that not more than 45 to 50% of the alumina can be removed from the zeolite although removal of calcium is nearly complete. A continuous flow column procedure would be expected to give similar results.

- 30 The above data also indicate that maximum removal of alumina and the zeolite cation can be effected through treatment of the zeolite with successive batches of fresh chelating solution.

- 35 Examples 5—9 will demonstrate that EDTA can be used directly as a method to increase the SiO₂/Al₂O₃ ratio substantially in crystal-

line aluminosilicates of the NaY type. This is accomplished without seriously destroying or effecting the adsorptive and crystalline properties. 40

EXAMPLE 5:

The starting material (utilized in the runs of Examples 6—9), containing 9.6 wt. % Na, 19.6 wt. % Al₂O₃, and 66.8 wt. % SiO₂, had the basic formula 0.923 Na₂O.Al₂O₃.5.8 SiO₂ and had a cyclohexane adsorption of 19.7 wt. %. Characterized by X-ray analysis, this material had a lattice constant of a₀ 24.61 Å. 45

This material (NaY) is identified as Example 5 in Table E.

EXAMPLES 6—9:

5 Examples 6, 7, 8 and 9 (data for which is set forth in Table E) were prepared by successive treatments of 1/2 lb. of the above NaY containing 60% solids with 20 g. portions of EDTA each in 200 cc. H₂O for 24 hours at 200°F. The total EDTA used was equivalent to 2 times the theoretical necessary to form Tetra Na EDTA. After each contact the sample was filtered and washed with an equal volume of water. Samples were taken after each contact for adsorption, composition and X-ray analysis.

EXAMPLES 10—14:

20 In Examples 6—9, a high silica NaY aluminosilicate (5.8 SiO₂:Al₂O₃) was used as the starting material. Examples 11—14 demonstrate that similar increases in SiO₂/Al₂O₃ ratios may be obtained from successive treatments of a low silica NaY aluminosilicate (4.37 SiO₂/Al₂O₃) with EDTA. A description of the details of these examples is set forth in Table E'.

25 As will be seen in Table E', in this preparation, the SiO₂/Al₂O₃ ratio was not increased as much as in the high silica NaY run of Examples 5—9. Similarly to the runs of
30 Examples 5—9, the X-ray data for Examples

11—14 show an increase in unit cell dimension from a_0 24.66 Å° to a_0 24.69 Å°, then progressive decrease to a_0 24.60 Å°. The adsorptive properties in this series also show increased cyclohexane adsorption after the first contact, then progressive decline to 13.2 wt. % cyclohexane adsorption.

35 These results were unexpected since EDTA is not soluble in water and is assumed to be too large to go into the aluminosilicate structure. The analytical data substantiate the fact that chelation has occurred since both sodium and alumina were reduced. Although the solution pH in this process is low (about 3.6 to 4.7), no serious damage to crystallinity occurs. This can be explained by the limited reactivity of the EDTA due to its limited solubility.

40 The described process of contacting crystalline aluminosilicate with EDTA for control of SiO₂/Al₂O₃ ratio can be applied easily to a commercial process. The resulting sodium alumina chelate can be decomposed by heating in a caustic solution, precipitating out the insoluble alumina. It may also be possible to strongly acidify the sodium alumina chelate to form the insoluble tetrahydrogen EDTA. The resulting soluble sodium EDTA can be converted to insoluble EDTA simply by acidifying with any acid. The recovered EDTA can thus be recycled for additional chelation. Recovery of the chelating agents used in the other examples described herein may be similarly effected.

TABLE E

EDTA Modifications of Y Aluminosilicates⁽¹⁾

Example No.	5	6	7	8	9
Description	Base: High-SiO ₂ NaY (5.8 SiO ₂ /Al ₂ O ₃)				
Processing					
NaY (wt. lbs.)	1/2 lb	-----	-----	-----	>
EDTA, wt. g.		20	-----	-----	>
Temp., °F		200	-----	-----	>
Contact, Hrs.		24	-----	-----	>
Composition as Analyzed					
Na, Wt. %	9.6	7.5	6.3	5.1	3.2
Al ₂ O ₃ , Wt. %	19.6	17.2	14	11.4	8.1
SiO ₂ , Wt. %	66.8	71	75	80.8	85.7
Na ₂ O/SiO ₂ M ratio	0.188	0.138	0.11	0.089	0.0485
Na ₂ O/Al ₂ O ₃ M ratio	1.085	0.965	1.00	1.00	0.875
SiO ₂ /Al ₂ O ₃ M ratio	5.8	7.04	9.12	12	18
Adsorption					
Cyclohexane, Wt. %	19.7	20.5	19.5	17.3	15.4
X-ray Analyses					
Lattice Constant a ₀ (Å)	24.61	24.63	24.60	24.55	24.58

(1) Processing was by successive treatments of EDTA. Thus, Example 9 had four treatments with 20 g. EDTA.

TABLE E'
EDTA Modifications of Y Aluminosilicates⁽¹⁾

Example No.	10	11	12	13	14
Description	Base: Low-SiO ₂ NaY (4.37 SiO ₂ /Al ₂ O ₃)				
Processing					
NaY (wt. lbs.)	1/2 lb	-----	-----	-----	-----
EDTA, wt. g.		20	-----	-----	-----
Temp., °F		200	-----	-----	-----
Contact, Hrs.		24	-----	-----	-----
Composition as Analyzed					
Na, Wt. %	10.7	9.9	8.6	6.8	5.2
Al ₂ O ₃ , Wt. %	23.7	21.1	18.8	17.0	12.7
SiO ₂ , Wt. %	60.9	65.1	69.4	73.5	79.0
Na ₂ O/SiO ₂ M ratio	0.229	0.200	0.162	0.120	0.0856
Na ₂ O/Al ₂ O ₃ M ratio	1.00	1.05	1.02	0.887	0.908
SiO ₂ /Al ₂ O ₃ M ratio	4.37	5.25	6.25	7.34	10.5
Adsorption					
Cyclohexane, Wt. %	20.1	20.7	19.9	18.0	13.2
X-ray Analyses					
Lattice Constant a ₀ (Å)	24.66	24.69	24.63	24.61	24.60

(1) Processing was by successive treatments of EDTA. Thus, Example 14 had four treatments with 20 g. EDTA.

EXAMPLE 15: This example will serve to illustrate that the EDTA method of alumina chelation for increased SiO₂/Al₂O₃ ratio can be applied to an NaX type crystalline aluminosilicate.

Example 15 was prepared by contacting 1/2 lb. wet cake (60% solid) of commercial NaX aluminosilicate (13X) twice with 25.1 g. EDTA in 200 cc H₂O for 24 hours at 200°F. in each contact. The pH off was 5.7. Cyclohexane adsorption and X-ray analysis show

that the SiO₂/Al₂O₃ ratio can be increased in NaX to 3.06 without seriously damaging the crystallinity. [Note: crystallinity as used in this specification is determined by comparison with a commercial 4A aluminosilicate as standard 100% crystalline.]

TABLE F
Chelation with EDTA

Example No.	15
Base Material Type	NaX
Composition	
Na, Wt. %	14.3
Al ₂ O ₃ , Wt. %	31.6
SiO ₂ , Wt. %	47.1
SiO ₂ /Al ₂ O ₃ M Ratio	2.53
Adsorption	
Cyclohexane, Wt. %	17.9
X-ray Analysis	
Crystallinity, %	90
Composition of Treated Catalyst	
Na, Wt. %	12.0
Al ₂ O ₃ , Wt. %	29.1
SiO ₂ , Wt. %	52.0
SiO ₂ /Al ₂ O ₃ M ratio	3.06
Adsorption	
Cyclohexane, Wt. %	16.1
X-ray	
Crystallinity, %	75

- 5 [Note: The resulting aluminosilicate in the run of Example 15 contains a slight amount of form "P" aluminosilicate in addition to the NaX form. When used in this specification, "pH Off" designates the pH of the solution after contact with the aluminosilicate; "pH On" before such contact.]

EXAMPLES 16—20:

- 10 These examples (the results and details of which are shown in Table G) will serve to demonstrate that ammonium salts of chelating agents can also function as desired, increasing the SiO₂/Al₂O₃ ratio in crystalline aluminosilicates. In addition, these chelating salts also exchange the residual sodium to form ammonium forms of the aluminosilicates.

Examples 16 and 17 were respectively conducted by contacting low silica NaY (4.52 SiO₂/Al₂O₃) and a high silica NaY (6.15 SiO₂/Al₂O₃) for 4 contacts each at 200°F. for 24 hours using 20 g. EDTA + NH₄OH to form the (NH₄)₂H₂ EDTA chelating agent.

Example 18 demonstrates that NaX can be treated in like manner without serious reduction in adsorptive properties.

Examples 19 and 20 show that either ammonium acid EDTA or ammonium acid citrate can function in similar manner forming acid crystalline aluminosilicate which can absorb normal hexane and is stable to tempering up to 650°F. for the period of pretreatment in the adsorption test. The water adsorption was not seriously affected.

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25

30

TABLE G
Chelation with Ammonium Chelating Salts

Example No.	16	17	18	19	20
Base Material					
Type	NaY	NaY	NaX	NaA	NaA
Composition					
Na, Wt. %	9.7	9.6	14.3	15.3	15.3
Al ₂ O ₃ , Wt. %	23.5	19.0	31.6	34.7	34.7
SiO ₂ , Wt. %	62.6	68.7	47.1	40.9	40.9
SiO ₂ /Al ₂ O ₃ M ratio	4.52	6.15	2.53	2.0	2.0
Adsorption					
Cyclohexane, Wt. %	20.4	19.3	17.9		
X-ray Analysis					
Lattice Constant a ₀ (Å)	24.66	24.58	24.96		
Chelation Reaction					
Wt. Base, Lb	1/2	1/2	1/2	1/2	
% Solids	60	60	60	100	
Contacting Solution					
EDTA, g	20	20	28.9	29.95	[Ammonium acid citrate 19.4]
NH ₄ OH g (l)	8	8	11.85	11.95	18.5
H ₂ Occ	200	200	200	400	400
No. Contacts	4	4	4	4	4
Temp. Contacts	200	200	200	200	200
pH On	—	—	—	5.7	6.1
pH Off	6.1—5.5	5.8—5.6	7.7—6.5	5.7	6.1
Composition of Treated Catalyst					
Na, Wt. %	4.0	2.8	7.3	10.1	9.08
Al ₂ O ₃ , Wt. %	22.6	19.6	33.2	36.6	37.8
SiO ₂ , Wt. %	73.5	74.8	54.7	47.7	47.11
SiO ₂ /Al ₂ O ₃ M Ratio	5.55	6.45	2.81	2.22	2.11

(1) Concentrated aqueous ammonia in amount to give the diammonia salt.

TABLE G (continued)

Example No.	16	17	18	19	20
Adsorption					
Cyclohexane, Wt. %	20.8	19.8	15.2	0.7 Cyclohexane 4.6 n-hexane	0.5
H ₂ O, Wt. %				26.9	27.5
X-ray					
Lattice Constant a ₀ (Å)	24.66	24.58	24.91		

5 The high catalytic activities obtained by aluminosilicate compositions prepared in accordance with the present invention can be readily illustrated in connection with the cracking of a representative hydrocarbon charge. In a number of the examples hereinafter set forth, the reference catalyst employed consisted of a conventional silica-alumina "bead" type cracking catalyst. The silica-alumina catalyst contained about 10 weight percent Al₂O₃ and the remainder SiO₂. In some instances, it also contained a trace amount of Cr₂O₃, i.e., about 0.15 weight percent.

10 The cracking activity of the catalyst is further illustrated by its ability to catalyze the conversion of a Mid-Continent Gas Oil having a boiling range of 450—950°F. to gasoline having an end point of 410°F. Vapors of the gas oil are passed through the catalyst at temperatures of 875°F. or 900°F. substantially at atmospheric pressure at a feed rate of 2.0 to 16 volumes of liquid oil per volume of catalyst per hour for ten minutes. The method of measuring the instant catalyst was to compare the various product yields obtained with such catalyst with yields of the same products given by conventional silica-aluminum catalysts at the same conversion level and at the same temperature. The differences (Δ values) shown hereinafter represent the yields given by the present catalyst minus yields given by the conventional catalyst. In these tests, the catalyst compositions of the invention were precalcined at about 1000°F. prior to their evaluation as a cracking catalyst.

EXAMPLES 21—24:

40 These examples (the details and results of which are set forth in Tables H and I), illustrate the catalytic advantages obtained by pre-treating a sodium aluminosilicate with a chelating agent such as EDTA to increase the SiO₂/Al₂O₃ mole ratio, prior to exchange with cations, i.e., with rare earth ions.

Examples 21 and 22 were prepared by continuously base exchanging the aluminosilicate product of Examples 14 and 9 with a combined solution of 5% RECl₃·6H₂O + 2% NH₄Cl, reducing the residual sodium to 0.47 wt. % Na with the low silica NaY (Ex. 9) and to 0.24 wt. % with the high silica NaY (Ex. 14). The catalysts were then washed, dried, pelleted to a size of 4 × 10 mesh, tempered 10 hours at 1000°F. and steam treated 24 hours at 1200°F. with 100% steam at 15 psig. [Note: unless otherwise indicated, RECl₃ when used in this specification shall refer to a mixture of rare earth chlorides consisting essentially of the chlorides of lanthanum, cerium, neodymium and praseodymium, with minor amounts of samarium, gadolinium and yttrium. A rare earth chloride solution containing such mixture is commercially available and it contains the chlorides of a rare earth mixture having the relative composition: cerium (as CeO₂) 48% by weight; lanthanum (as La₂O₃) 24% by weight; praseodymium (as Pr₆O₁₁) 5% by weight; neodymium (as Nd₂O₃) 17% by weight; samarium (as Sm₂O₃) 3% by weight; gadolinium (as Gd₂O₃) 2% by weight; yttrium (as Y₂O₃) 0.2% by weight; and other rare earth oxides 0.8% by weight. Similarly, the cation "RE" shall be construed to cover the same mixture of rare earth cations unless otherwise specified.]

Analytical data summarized in Table H show that the aluminosilicate of Example 14 could be base exchanged with a combined solution of 5% RECl₃·6H₂O + 2% NH₄Cl using the equivalent of 36 2-hour contacts with 1 volume solution per volume slurry. The final catalyst (Ex. 21) has a residual sodium content of 0.47 wt. % (RE)₂O₃ content of 9.9 wt. %, Al₂O₃ content of 14.8 wt. % and SiO₂ content of 74.9 wt. %. The final SiO₂/Al₂O₃ ratio was 8.6/1.

Catalytic data on the steam catalyst indicated that this catalyst was quite active (64.8

- vol. % conversion at 16 LHSV in the standard gas oil cracking test), indicating a superior initial selectivity. [Note: "LHSV" designates the liquid hourly space velocity.]
- 5 Example 22 was prepared in the same manner as Ex. 21 except that the starting base was that of Ex. 9, which had a starting $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 18/1.
- 10 The final catalyst analyzed 0.24 wt. % Na, 6.7% $(\text{RE})_2\text{O}_3$; 7.4 wt. % Al_2O_3 , and 84.6 wt. % SiO_2 . The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio in the product was 19.5/1. It is clearly evident that a substantial amount of alumina was chelated from the crystalline structure. Even
- 15 at this degree, the catalyst was quite active (50.2 vol. % conversion at 16 LHSV in the standard gas oil cracking test) and had excellent selectivity advantages over standard silica-alumina cracking catalyst at the same conver-
- 20 sion (+8.9 vol. % C_3 + gasoline).

These data clearly show that a wide variety of aluminosilicates are possible with controlled chelation of the crystalline alumina.

Examples 23 and 24 were prepared respectively by pretreating Y aluminosilicates as described in Examples 12 and 7: contacting the low silica and high silica NaY twice with EDTA at 200°F. for 24 hours and then base exchanging with rare earth and ammonium chloride solution as described in Examples 21 and 22. These materials were then further processed as described in Examples 21 and 22. The residual sodium content was 0.8 wt. % in the case of the low silica NaY (Ex. 24) and 1.13% when using the high silica NaY (Ex. 23). The corresponding $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios were 5.95/1 and 7.25/1, respectively. Again, catalytic results on the final materials were excellent.

TABLE H
Undiluted Catalyst Preparation

Example No.	21	22
Description	(1)	(2)
Base Exchange		
Solution	$\text{RECl}_3 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{Cl}$	
Conc. Wt. %	5	2
Contact	90 lbs. per 1/2 lb. at 180°F. for 3 days	
Composition of Treated Catalyst		
Na, Wt. %	0.47	0.24
(RE) ₂ O ₃ , Wt. %	9.9	6.7
Al ₂ O ₃ , Wt. %	14.8	7.4
SiO ₂ , Wt. %	74.9	84.6
SiO ₂ /Al ₂ O ₃ M Ratio	8.6	19.5
Physical Properties (Fresh Catalyst)		
App. Dens. g/cc	0.59	0.56
Surface Area, m ² /g	429	390
Adsorption—Cyclohexane Wt. %	11.2	9.0
Catalytic Evaluation (Steamed)		
Conditions—LHSV	16	16
—C/O	0.38	0.38
Conversion, Vol. %	63.6	50.2
10 RVP Gaso. Vol. %	59.3	48.9
Excess C ₄ 's, Vol. %	9.6	5.9
C ₅ + Gasoline, Vol. %	56.3	46.1
Total C ₄ 's, Vol. %	12.7	8.8
Dry Gas, Wt. %	5.0	3.9

TABLE H (continued)

Example No.	21	22
Coke, Wt. %	1.15	0.57
H ₂ , Wt. %	0.01	0.01
Delta Advantage over Si/Al		
10 RVP, Gasol., Vol. %	+13.0	+9.6
Excess C ₄ 's, Vol. %	-5.4	-4.3
C ₅ + Gasoline, Vol. %	+12.1	+8.9
Total C ₄ 's, Vol. %	-4.3	-3.7
Dry Gas, Wt. %	-3.0	-1.9
Coke, Wt. %	-3.0	-2.3

(1) NaY treated as described in Example 14 for 4 contacts with EDTA, increasing the SiO₂/Al₂O₃ to 10.5/1; cyclohexane adsorption, wt. %: 13.3; X-ray: lattice cell constant a₀ of 24.60 Å°.

(2) NaY treated as described in Example 9 for 4 contacts with EDTA, increasing SiO₂/Al₂O₃ to 18/1; cyclohexane adsorption, wt. %: 15.4; X-ray: lattice cell constant a₀ 24.46 Å°.

[Note: Where denoted "steamed" (here and elsewhere in this specification), the catalyst has been treated with 100% steam at 1200F° and 15 psig for 24 hours. The symbol "C/O" designates catalyst/oil ratio.]

TABLE I
Undiluted Catalyst Preparation

Example No.	23	24
Description	(1)	(2)
Base Exchange		
Solution	$\text{RECl}_3 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{Cl}$	
Conc., Wt. %	5	2
Contacts	90 lbs. per lb. at 180°F. ----->	
Compositions of Treated Catalyst		
Na, Wt. %	0.8	1.13
(RE) ₂ O ₃ , Wt. %	6.8	5.13
Al ₂ O ₃ , Wt. %	20.7	14.8
SiO ₂ , Wt. %	62.9	72.7

TABLE I (continued)

Example No.	23		24	
Description	(1)		(2)	
Physical Properties (Fresh Catalyst)				
App. Dens. g/cc	0.38		0.38	
Adsorption—Cyclohexane, Wt. %	21.7 ⁽⁴⁾	17.2 ⁽³⁾	17.7 ⁽²⁾	14.3 ⁽³⁾
X-ray Analysis				
Lattice Cell Constant a_0 (Å)	24.64		24.58	
Catalytic Evaluation (Steamed Catalyst)				
Conditions—LHSV	16		16	
—C/O	0.38		0.38	
Conditions				
Conversion, Vol. %	66.5		61.5	
10 RVP Gaso., Vol. %	61.6		60.0	
Excess C ₄ 's, Vol. %	10.7		7.8	
C ₅ +Gasoline, Vol. %	58.6		56.5	
Total C ₄ 's, Vol. %	13.2		11.3	
Dry Gas, Wt. %	5.3		3.8	
Coke, Wt. %	1.45		1.0	
H ₂ , Wt. %	0.01		0.01	
Delta Advantage over Si/Al				
10 RVP, Gaso., Vol. %	+13.9		+14.8	
Excess C ₄ 's, Vol. %	-6.0		-6.4	
C ₅ +Gasoline, Vol. %	+13.0		+13.4	
Total C ₄ 's, Vol. %	-4.8		-4.9	
Dry Gas, Wt. %	-3.2		-3.8	
Coke, Wt. %	-5.2		-3.7	

Notes to Table I

(1) Prepare as described in Example 12: Na, 8.0 wt. %; Al_2O_3 , 19.4 wt. %; SiO_2 , 68.0 wt. %; $\text{SiO}_2/\text{Al}_2\text{O}_3$, 5.95 wt. %; cyclohexane adsorption, wt. %: 21.7.

(2) Prepare as described in Example 7: Na, 7.0 wt. %; Al_2O_3 , 17.9 wt. %; SiO_2 , 76.3 wt. %; $\text{SiO}_2/\text{Al}_2\text{O}_3$, 7.25; cyclohexane adsorption, wt. %: 17.7.

(3) Finished catalyst.

Examples 25—27 demonstrate the effectiveness of EDTA treatment on calcium and rare earth exchanged aluminosilicate.

EXAMPLE 25:

This example was prepared by EDTA treating a CaHY aluminosilicate (dried at 230°F.) containing 1.4 wt. % Na, 24.3 wt. % Al_2O_3 , 6.8 wt. % Ca, and 63.6 wt. % SiO_2 and having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 4.67/1 and X-ray lattice constant a_0 of 24.64 Å. EDTA treatment consisted of contacting 1/4 lb. of the CaHY base with 2 contacts of 20 g. EDTA in 200 cc H_2O each for 24 hours at 200°F. The treated material was washed, dried at 230°F., pelleted and sized to 4/10 mesh (Tyler), tempered at 1000°F., and steam treated for 24 hours at 1200°F. with 15 psig steam.

The final catalyst analyzed 1.43 wt. % Na, 20 wt. % Al_2O_3 , 70.7 wt. % SiO_2 , 5.2 wt. % Ca, and had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 6.05/1 and a X-ray lattice constant a_0 of 24.64 Å.

Catalytic data show that this catalyst had improved selectivity after the alumina chelation treatment, as measured by vol. % C_3 + gasoline production. The improvement was about 2 vol. % more C_3 + gasoline yield. However, a 3 vol. % decrease in the standard gas oil cracking test activity at 16 LHSV was noted.

EXAMPLE 26:

Preparation of this example was accomplished by treating a REHY aluminosilicate with EDTA in the same manner as described in Example 25. In this preparation, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio was increased from 4.5/1 to 6.05/1. In this process, the rare earth content was only decreased slightly from 14.8 to 13.4 wt. % in the final catalyst. In addition to the rare earth decrease, the residual sodium content was decreased from 1.36 to 1.01 wt. %. The X-ray lattice constant a_0 changed from 24.7 to 24.52 Å.

Catalytic evaluation of this catalyst also shows that it is catalytically advantageous in C_3 + gasoline yield to treat a REHY catalyst

with a complexing agent. The catalyst was less active (59.6 vol. % conversion at 16 LHSV in the standard gas oil cracking test, compared to 66.1 for the original REHY). The C_3 + gasoline yield was increased from +10.5 to +12.4 vol. % over standard Si/Al catalysts. The coke advantage is also obvious, showing a decrease from 2.2 wt. % to 0.8 wt. %. This type of coke decrease is typical for the EDTA-treated rare earth catalysts.

In both examples, the gain in selectivity was about +2 vol. % C_3 + gasoline advantage over the untreated CaHY and REHY catalyst at a lower conversion.

EXAMPLE 27:

Preparation of this example was accomplished by treating a CaHY aluminosilicate with a complex ammonium EDTA, di(tetraethylammonium) dihydrogen EDTA (see Examples 2—4). This run involved the treatment of 70 g. of CaHY with 4 successive treatments each for at least 16 hour duration at reflux (100°C.). Each contact was with 260 ml. of solution prepared by treating 52.6 g. EDTA with sufficient quaternary ammonium hydroxide so that the solution is about 1.4 N based on tetraethylammonium ion. The treated material was further water washed with 200 ml of water.

At this point, the product having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 6.78 also had an increased sodium content of 4.39 mol. % due to the sodium in the complex ammonium EDTA. It was necessary to base exchange this catalyst again with calcium-ammonium chloride to exchange the sodium. The complex ammonium EDTA treatment also almost completely extracted the initial calcium present.

The final calcium catalyst analyzed 0.14 wt. % Na, 19.6 wt. % Al_2O_3 , 71.8 wt. % SiO_2 , 6.4 wt. % Ca and had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 6.22 and a X-ray lattice constant a_0 of 24.64 Å.

Catalytic data show that the complex ammonium EDTA treatment was not only beneficial in selectivity but also in activity, giving a +12.9 vol. % C_3 + gasoline advantage over

standard Si/Al and also a 72.1 vol. % conversion at 10 LHSV in the standard gas oil cracking test.

EXAMPLE 28:

5 This example demonstrates that an aluminosilicate can first be pre-treated with a complexing agent to remove alumina and then base
10 exchanged with a divalent cation of the calcium type in combination with ammonium. This preparation started with the treatment of 4 lbs of high silica NaY aluminosilicate (6.3 SiO₂/Al₂O₃)
15 twice with 160 g. EDTA in 1600 cc H₂O at 200°F. for 24 hours each. After this treatment, the SiO₂/Al₂O₃ mole ratio was 8.6/1. One-half pound of the above aluminosilicate was treated continuously at 180°F. with 90 lbs. of combined 5% CaCl₂—2%—NH₄Cl for 3 days followed by water wash,
20 drying at 230°F., pelleting and sizing to 4/10 mesh (Tyler), tempering and then steam treating for 24 hours at 1200°F. with 15 psig steam.

The final catalyst analyzed 0.8 wt. % Na, 6.99 wt. % Ca and a SiO₂/Al₂O₃ mole ratio of 7.25/1 and had a X-ray lattice constant a₀ of 24.61 Å.

25 The standard gas oil cracking evaluation at 10 LHSV of the steamed catalyst shows this catalyst to be very active (70.9 vol. % conversion) and very selective (+12.6 vol. % C₃ + gasoline more than standard Si/Al at the same conversion).

EXAMPLE 29:

35 This example demonstrates that an acid Y aluminosilicate having excellent catalytic properties can be made in the same manner as described in Example 28.

Two pounds of high silica NaY aluminosilicate was contacted twice with 80 g. EDTA in 800 cc H₂O for 24 hours at 200°F. This treatment increased the SiO₂/Al₂O₃ molar ratio from 6.3/1 to 10/1. One-half pound of this aluminosilicate was then treated 4 times with (NH₄)₂H₂EDTA at 200°F. using 40 g. EDTA + NH₄OH per contact. Three of these
45 contacts were for 24 hour duration and one was for 72 hours. The treated aluminosilicate was washed, dried at 200°F, pelleted and sized to 4/10 mesh, tempered and then steam
50 treated for 24 hours at 1200°F. with 15 psig steam.

The final catalyst analyzed Na, 1.5 wt. %; Al₂O₃ 13.1 wt. %; SiO₂ 86.1 wt. %. The final SiO₂/Al₂O₃ molar ratio was 11.1/1. The
55 X-ray lattice constant a₀ was 24.58 Å.

Standard gas oil cracking test data shows that this acid Y aluminosilicate is active at 10 LHSV (51.3 vol. % conversion) and is selective, giving an advantage of +9.0 vol. %
60 C₃ + gasoline over standard Si/Al.

EXAMPLE 30:

This preparation serves to demonstrate a process of combining a complexing agent with cation exchanger and ammonium. The complexing agent was EDTA and the cation exchanger was manganese.

The exchange process consisted of contacting 1/2 lb of high silica NaY aluminosilicates (6.3/1 SiO₂/Al₂O₃) 8 times with 200 cc solution of manganese chloride, EDTA, NH₄OH and HCl to form the equivalent of 0.343 molar ammonium acid manganese EDTA with the pH adjusted to 5.5 with HCl. Six of the contacts were for 24 hour duration and 2 were for 96 hours, all at 200°F.

The final catalyst analyzed 1.0 wt. % Na, 2.75 wt. % Mn, 17.8 wt. % Al₂O₃, 76.2 wt. % SiO₂, while the SiO₂/Al₂O₃ molar ratio was increased to 7.25/1. The X-ray lattice constant a₀ was 24.61 Å.

Catalytic data show the particular catalytic advantages of the complex treatment which increased the SiO₂/Al₂O₃ ratio at the same time Mn⁺⁺ was exchanged into the structure. This catalyst was very active (65.9 vol. % conversion at 10 LHSV in the standard gas oil cracking test) and gave +12.9 vol. % more C₃ + gasoline advantage over standard Si/Al catalyst.

EXAMPLES 31—33:

90 These examples were prepared to demonstrate the fact that the SiO₂/Al₂O₃ molar ratio could be increased considerably (11/1) with a complexing agent that removes alumina without seriously affecting the structure. The aluminosilicates thus prepared can then be exchanged with acidic salts such as Al(NO₃)₃, Fe(NO₃)₃ and MnCl₂ directly without severe effect on the structure. It appears that one can exchange the residual sodium from an EDTA treated aluminosilicate with Al⁺⁺⁺, Fe⁺⁺⁺ and Mn⁺⁺ to form ferric-aluminosilicates and manganese aluminosilicate.

Example 31 was prepared by base exchanging 150 g. of the EDTA treated aluminosilicate for eight 2 hour contacts with a 2% Al(NO₃)₃·9H₂O solution. At the end of this exchange this preparation had a residual Na content of 1.78 wt. % and a cyclohexane adsorption of 12.9, substantiating the fact that the aluminosilicate retained most of its adsorptive properties.

Example 32 was prepared in essentially the same manner as Example 31 except that the EDTA treated aluminosilicate was treated with a 2% Fe(NO₃)₃·9H₂O. After the eight 2 hour contacts with 2% Fe(NO₃)₃·9H₂O, the residual sodium content was 1.5 wt. %, Al₂O₃ 11.9 wt. %, SiO₂ 75.9 wt. %, Fe₂O₃ 7.89 wt. %, while the SiO₂/Al₂O₃ mole ratio was 10.8/1. Cyclohexane adsorption data show this catalyst to have 11.4 wt. % adsorption.

In like manner, Example 33 was prepared

base exchanging only with 2% $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. Even though the residual sodium was decreased to 1.87%, the cyclohexane data (18.5 wt. %) show that the Mn exchange does not affect the adsorption properties of the EDTA treated aluminosilicate.

It is to be noted that by virtue of the present invention, cations which hydrolyze to form an acidic solution can be used readily and successfully to exchange the remaining residual sodium in the aluminosilicate. This results from the fact that as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is increased, it becomes possible to exchange cations with more acidic solution. If the $\text{SiO}_2/\text{Al}_2\text{O}_3$ is increased sufficiently (viz., above about 7 $\text{SiO}_2/\text{Al}_2\text{O}_3$) it will be possible to make a wide variety of aluminosilicates since these aluminosilicates can be exchanged at lower pH.

EXAMPLES 34—40:

These examples, summarized in Table J and K, involve the treatment of Durabead-type catalyst materials prepared by incorporating, in one series (Examples 34—38), 10 wt. % of EDTA-treated NaY aluminosilicate (8.6/1 $\text{SiO}_2/\text{Al}_2\text{O}_3$) and, in the second series (Examples 39 and 40), the same NaY aluminosilicate after pre-exchanging with rare earth and ammonium chlorides.

The Durabead preparation is made by dispersing the aluminosilicate along with McNamee clay in a silicate solution which is gelled with an acid alum solution to form a 94% SiO_2 —6% Al_2O_3 matrix. These bead catalysts were formed at 8.5 pH and, immediately thereafter, base exchanged with didymium followed by NH_4Cl (Ex. 34), NH_4Cl (Ex. 35), MnCl_2 (Ex. 36), Mg (Ex. 37) and Ca (Ex. 38). [Note: a more complete description of Durabead-type catalysts may be found in U.S. Specification No. 2,900,349, whose disclosure is hereby incorporated by reference].

As shown by the catalytic data (the standard gas oil cracking test at 4 LHSV after steaming) presented in Table J, all of these catalysts were very active and extremely selective.

Example 35 is an acid Y Durabead which is quite selective for having been exchanged only with NH_4Cl .

Data with respect to the catalyst of Examples 39 and 40 are presented in Table K. These catalysts were prepared by the pre-exchange method followed by only $(\text{NH}_4)_2\text{SO}_4$ exchange in Example 39 and CaCl_2 exchange in Example 40. Both of these catalysts were active and very selective for gas oil cracking as shown in the standard gas oil cracking test at 4 LHSV.

TABLE J
Durabead Catalysts Prepared with the EDTA Treated NaY

Example No.	34	35	36	37	38
Description					
Matrix	Si/Al(94% SiO ₂ —6% Al ₂ O ₃) ----->				
Fines					
(1) Type	EDTA Treated NaY (SiO ₂ /Al ₂ O ₃ 8·6/1)				
Conc., wt. %	10 ----->				
(2) Type	McNamee Clay ----->				
Conc., wt. %	15 ----->				
Base Exchange					
Solution	(1) DiCl ₃ ·6H ₂ O	NH ₄ Cl	MnCl ₂	MgCl ₂	CaCl ₂
Conc., wt. %	(2)	1	2	2	2
Contacts	(2)	(3)	(3)	(3)	(3)
Composition					
Na, Wt. %	0·2	0·2	0·4	0·4	0·2
(RE) ₂ O ₃ , wt. %	4·6				
Mn, wt. %			4·65		
Mg, wt. %				3·6	
Ca, wt. %					2·7
Physical Properties of Treated Catalyst					
Steamed Surface Area, m ² /g	165	116	148	174	166
Catalytic Evaluation					
Conditions—LHSV	4 ----->				
—C/O	1·5 ----->				
Conv., vol. %	67·3	53·7	58·6	63·2	62·0
10 RVP Gaso., vol. %	58·8	48·0	54·0	55·9	55·4
Excess C ₄ 's, vol. %	12·2	9·4	8·6	11·5	9·9

TABLE J (continued)

Example No.	34	35	36	37	38
Catalytic Evaluation					
C ₃ + Gasoline, Vol. %	56.0	45.1	51.2	53.1	52.7
Total C ₄ 's, vol. %	15.1	12.2	11.4	14.3	12.7
Dry Gas, wt. %	6.8	5.2	4.8	5.7	6.0
Coke, wt. %	1.53	0.9	1.5	1.8	1.4
H ₂ , wt. %	0.04	0.04	0.06	0.04	0.03
Delta Advantage Over Si/Al					
10 RVP, Gasol., vol. %	+10.8	+6.9	+10.3	+9.9	+9.9
Excess C ₄ 's, vol. %	-4.4	-2.0	-4.5	-3.4	-4.5
C ₃ + Gasoline, vol. %	+10.0	+6.1	+9.5	+9.1	+9.3
Total C ₄ 's, vol. %	-3.3	-1.4	-3.7	-2.6	-3.7
Dry Gas, wt. %	-1.8	-1.2	-2.3	-2.2	-1.7
Coke, wt. %	-4.5	-2.6	-2.8	-3.3	-3.5

(1) DiCl_3 , didymium chloride, is a mixture of rare earth chlorides having a low cerium content. It consists of the following rare earths determined as oxides: lanthanum, 45—46% by weight; cerium, 1—2% by weight; praseodymium, 9—10% by weight; neodymium, 32—33% by weight; samarium, 5—6% by weight; gadolinium, 3—4% by weight; yttrium, 0.4% by weight; other rare earths, 1—2% by weight.

(2) The run of Ex. 34 involved the contacting the aluminosilicate with a 2% solution

of $\text{DiCl}_3 \cdot 6\text{H}_2\text{O}$ for one 16 hour treatment followed by one 24 hour continuous treatment with 1% NH_4Cl . [Note: Where the contact of an aluminosilicate by a treating solution is indicated to be "continuous" or otherwise similarly designated, this refers to a flowing system equivalent to one-half volume of solution per volume of catalyst per hour.]

(3) The runs of Exs. 35—38 involved continuous contacting of the aluminosilicate with a base exchange solution having the indicated concentration for one 24 hour period.

TABLE K

Durabead Catalysts Prepared with the Rare
Earth Pretreated EDTA Treated NaY

Example No.	39	40
Description		
Matrix	Si/Al(94%SiO ₂ -6%Al ₂ O ₃)	
Fines		
(1) Type	Rare Earth Exchanged EDTA Treated NaY	
Conc., wt. %	7	7
(2) Type	McNamee Clay	
Conc., wt. %	18	18
Base Exchange		
Solution	(NH ₄) ₂ SO ₄	CaCl ₂
Conc., wt. %	1.4	2
Contacts	1—24 hour continuous	
Composition		
Na, wt. %	0.4	0.5
(RE) ₂ O ₃ , wt. %	0.97	
Ca, wt. %		2.4
Physical Properties		
App. Dens., g/cc	0.83	0.74
Surface Area, m ² /g Steamed	111	167
Catalytic Evaluation		
Conditions—LHSV	4	4
—C/O	1.5	1.5
Conversion, vol. %	53.9	51.8
10 RVP Gasol., vol. %	48.7	47.8
Excess C ₄ 's, vol. %	9.0	7.0
C ₅ +Gasoline, vol. %	46.4	45.2
Total C ₄ 's, vol. %	11.3	9.7
Dry Gas, wt. %	4.8	4.9

TABLE K (continued)

Coke, wt. %	1-13	1-13
H ₂ , wt. %	0-04	0-04
Delta Advantage Over Si/Al		
C ₃ +Gasoline, vol. %	+7-9	+7-8
Total C ₄ 's, vol. %	-2-7	-3-7
Dry Gas, wt. %	-1-8	-1-4
Coke, wt. %	-2-4	-2-1

EXAMPLES 41 AND 42:

5 Still another approach made was to take advantage of the catalytic improvement possible with the complexing agent effect on catalysts. Here Durabead catalysts containing 10% high silica NaY aluminosilicate (6.25 SiO₂/Al₂O₃) with 15 wt. % McNamee clay for diffusivity in a 94% SiO₂-6% Al₂O₃ matrix were treated with EDTA first (44 g. EDTA/3 liters Durabead

hydrogel for 24 hours) and then base exchanged with (NH₄)₂SO₄ for one 24 hour treatment in Example 41, and with 2% RECl₃.6H₂O for one 16 hour treatment followed with NH₄Cl for one 24 hour treatment in Example 42.

Catalytic data presented in Table L clearly show the advantages in selectivity resulting from pretreating the hydrogel with EDTA in a pre-washing before base exchange.

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TABLE L

Durabead Catalyst Containing NaY Treated with EDTA

Example No.	41	42
Composition		
Na, wt. %	0.3	0.3
(RE) ₂ O ₃ , wt. %	—	1.13
Physical Properties		
App. Dens. g/cc	0.81	0.82
Surface Area, m ² /g. Steamed	98	121
Catalytic Evaluation		
Conditions—LHSV	4	4
—C/O	1.5	1.5
Conversion, vol. %	52.5	61.8
10 RVP Gaso., vol. %	45.4	55.2
Excess C ₄ 's, vol. %	10.6	10.8
C ₅ +Gasoline, vol. %	43.2	52.4
Total C ₄ 's, Vol. %	12.8	13.7
Dry Gas, wt. %	5.3	5.6
Coke, wt. %	1.4	1.4
H ₂ , wt. %	0.05	0.04
Delta Advantage Over Si/Al		
10 RVP, Gaso., vol. %	+4.9	+9.9
Excess C ₄ 's, vol. %	—0.4	—3.5
C ₅ +Gasoline, vol. %	+4.7	+9.2
Total C ₄ 's, vol. %	—0.4	—2.6
Dry Gas, wt. %	—0.9	—2.1
Coke, wt. %	—1.9	—2.1

EXAMPLE 43:

This example illustrates the applicability of the process of the present invention to still other aluminosilicates.

Example 43 was prepared by treating syn-

thetic chabazite with EDTA in the same manner as described before. The starting chabazite was prepared through the caustic-silicate fusion method. This method is carried out by reaction of 50 g. raw Dixie clay, a

- kaolinite, 81.7 g. NaOH, 536.0 g. "N" Brand silicate (28.5% SiO₂, 8.9% Na₂O, 62.6% H₂O) and 50 cc H₂O for 4 hours at 600°F. The resulting crusty solid was pulverized, then contacted first with 250 cc H₂O and then with 2628 cc of H₂O and digested for 21 hours at 200°F. The resulting crystalline material was separated from the supernatant liquid by filtering and washing. The starting composition was 9.9 wt. % Na, 22.7 wt. % Al₂O₃ and 63.3 wt. % SiO₂ and a starting SiO₂/Al₂O₃ mole ratio of 4.75/1. The cyclohexane adsorption was 0.8 wt. % and water adsorption 12.8 wt. %.
- One half pound of the synthetic chabazite was treated 4 times at 200°F. with 20 g. EDTA in 200 cc water. Three of the contacts were for 24 hour duration while one was for 72 hour duration.
- The treated chabazite had the following composition: 5.4 wt. % Na, 17.0 wt. % Al₂O₃, and 75.1 wt. % SiO₂. The SiO₂/Al₂O₃ mole ratio was increased to 7.5/1 by the EDTA chelation. The final treated chabazite had 5.8 wt. % cyclohexane, 6.2 wt. % normal hexane, and 16.8 wt. % H₂O adsorption, suggesting that the chabazite was activated to have superior adsorptive properties.

In an earlier part of this specification, it

was mentioned that disodium dihydrogen EDTA was ineffective to remove alumina from sodium zeolite Y due to the weak acid nature of the disodium dihydrogen EDTA. On the other hand, in Example 1, it was shown that the same chelating agent was effective to remove alumina from calcium zeolite Y, due to the highly stable calcium chelate which was formed and which provided the potential to cause the chelation reaction to take place. In Example 44, it will be shown that zeolites such as sodium zeolite Y can also be made alumina-deficient by treating with disodium dihydrogen EDTA providing the zeolite is given a preliminary acidification and solvolysis treatment.

EXAMPLE 44:

Samples of a sodium zeolite Y were exchanged with increasing amounts of NH₄⁺ ion and then calcined to give a series of sodium hydrogen zeolites in which the percent of hydrogen in cation sites varied from 40 to 68%. These materials were first contacted with water at room temperature overnight and then treated for 30—60 minutes with a solution of disodium dihydrogen EDTA. The products from these reactions were then analyzed for silica, alumina and sodium oxide. The results are summarized:

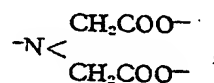
Percent Equivalents H initially in cation sites	Percent Equivalents Al removed
41	10
43	9
49	11
54	15
60	18
67	21
68	24

- As will be seen from the above, not only was aluminum chelated from the zeolite, but this test demonstrates that as the number of cation sites occupied by hydrogen is increased, the amount of aluminum removed by solvolysis (in this case, hydrolysis) from tetrahedral sites is also increased.

- Earlier in the present specification, it was pointed out that an extremely effective method of carrying out the present invention involved the use of sequestering agents which formed soluble complexes, which complexes could be readily removed from the solid alumina-deficient aluminosilicate by a simple filtration technique. It was also noted, however, that an alternative procedure contemplated the use of chelating materials which did not form soluble complexes but which nevertheless could be effectively separated from the alumina-deficient aluminosilicate. Such a technique is set forth in the following example:

EXAMPLE 45:

Dowex (Registered Trade Mark) ion exchange resin A—1 was used in this experiment. This material consists of a copolymer of styrene and 8% divinylbenzene. The functional group, an iminodiacetate



is located on aromatic rings and imparts to the resin chelating properties similar to those of ethylene-diaminetetraacetate. For example, the selectivity of the resin for Cu⁺⁺ versus Na⁺ is about 100 to 1.

Approximately 20 g. of a synthetic faujasite essentially in the calcium form, was slurried at room temperature for three days with 250 ml. of the chelating resin in the hydrogen form. The reaction product was separated from

- the resin beads by means of a U.S. Standard Sieve No. 100. The finely divided inorganic product was readily washed through the sieve while the beads were retained. The slurry of product and water which had passed through the sieve were filtered and the residue on the filter washed with water. The following summary of the properties of the initial zeolite and the product clearly shows the removal of aluminum from the zeolite:

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	Initial Zeolite	Product
Wt. %		
Na ₂ O	2.6	2.2
CaO	8.9	5.2
Al ₂ O ₃	21.7	18.5
SiO ₂	67.9	72.8
Mol %		
Na ₂ O	2.7	2.2
CaO	10.3	6.1
Al ₂ O ₃	13.8	11.9
SiO ₂	73.3	79.5
Molar Ratio SiO ₂ /Al ₂ O ₃	5.3	6.6
Cyclohexane sorbed, g./g. sample	0.185	0.193

- In carrying out the process of the present invention, care must be taken to avoid excessive treatment with the complexing agent to a point such that the crystallinity of the aluminosilicate is essentially destroyed. As will be apparent, the point at which this will take place will necessarily vary depending upon the aluminosilicate treated and the nature of the complexing agent, though such point may be readily determined in a given case by conventional techniques.

- While various theories have been postulated in earlier portions of the present specification for purposes of explaining the various inventive concepts heretofore described, it will be understood that such theories merely represent the present understanding of the inventors as to the phenomena involved and that the appended claims are not to be limited by such theories unless otherwise indicated.

- The catalysts prepared in accordance with the present invention find extensive utility particularly for transforming organic compounds which are catalytically convertible in the presence of acidic catalyst sites into modified organics. For example, they are useful in a wide variety of hydrocarbon conversion pro-

cesses including isomerization, dealkylation, alkylation, disproportionation, hydration of olefins, amination of olefins, hydrocarbon oxidation, dehydrogenation, dehydration of alcohols, desulfurization, hydrogenation, hydroforming, reforming, cracking hydrocracking, oxidation, polymerization, aromatization and the like. The catalysts are exceptionally stable and are particularly useful in such of the above and related processes carried out at temperatures ranging from ambient temperatures of 70°F. up to 1400°F., including such processes in which the catalyst is periodically regenerated by burning off combustible deposits. Because of their high catalytic activities, the catalysts are especially useful for effecting various hydrocarbon conversion processes such as alkylation, for example, at relatively low temperatures with small amounts of catalyst, thus providing a minimum of undesirable side reactions and operating costs.

By way of example, the dehydrogenation of hydrocarbons such as propane, butylene, butane, pentane, cyclopentane, cyclohexane, methyl cyclohexane and the like, can be carried out at temperatures ranging from about 300°F. to 1025°F. under atmospheric or superatmo-

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spheric pressures with a space velocity (LHSV) from 0.2 to 5000. For dehydrogenation, metals and oxides and sulfide of metals such as platinum, palladium, rhodium, tungsten, iron, copper or nickel can be employed as promoters with the active aluminosilicate.

For the desulfurization of hydrocarbons, which involves largely hydrogenation, the oxides and sulfides of such metals as cobalt, molybdenum, tungsten, chromium, iron, manganese, vanadium, copper and mixtures thereof as well as platinum group metals may be used in conjunction with the aluminosilicate. Desulfurization of shale distillates and the like may be carried out at temperatures between about 600°F. and 1000°F. under atmospheric or superatmospheric pressures with a space velocity (LHSV) between 0.2 and 50. The specific conditions within these ranges will vary with the feed stock undergoing desulfurization and the product desired.

The catalysts of the invention can be employed for hydrogenation of unsaturated aliphatic hydrocarbons, such as mono-olefins, diolefins, and the like, to form the corresponding saturated hydrocarbons, hydrogenation of unsaturated cyclic hydrocarbons, and hydrogenation of unsaturated alcohols, ketones, acids, etc. For hydrogenation reactions, the temperature may range up to 1000°F. under a pressure of about 10 to 3000 pounds p.s.i. or more, at a space velocity (LHSV) from about 0.5 to 5.0. The promoters which are normally employed with the aluminosilicate include the oxides of nickel, copper and iron and platinum group metals.

Hydrocracking of heavy petroleum residual stocks, cycle stocks, etc., may be carried out with active aluminosilicates promoted with about 0.05 to 10% by weight of a platinum metal such as platinum, palladium, rhodium, osmium, iridium, and ruthenium or with oxides or sulfides of metals such as cobalt, molybdenum, tungsten, chromium, iron, copper and the like. The petroleum feed stock is cracked in the presence of the catalyst at temperatures between 400°F. and 825°F. using molar ratios of hydrogen to hydrocarbon charge in a range between 2 and 80. The pressure employed will vary between 10 and 2500 psig and the space velocity between 0.1 and 10.

The catalysts of the invention may be further utilized for the alkylation of aromatic hydrocarbons or phenols and the conversion of olefinic, acetylenic and naphthenic hydrocarbons. Alkylation of aromatics and phenols may be carried out at temperatures between 15° and 850°F. under pressures of 0 to 1000 psig. The aromatizing reaction may be effected at temperatures between 350°F. and 1100°F. under atmospheric or elevated pressures. Other reactions in which the catalysts find utility include isomerization, polymerization, hydrogen transfer, oxidation of olefins to form the corresponding oxides (such as ethylene to

ethylene oxide, propylene to propylene oxide, etc.), as well as the oxidation of alcohols and ketones. The catalyst composition of the invention also finds utility in processes for the oxidation of cyclohexane to adipic acid through the precursors cyclohexanone and cyclohexanol, as well as in the manufacture of caprolactam from caprolactone and ammonia. Additionally, the catalyst composites of the invention may be useful catalytically in processes for the production of vinyl chloride by oxidative-dehydrogenation reactions involving ethane and hydrogen chloride.

WHAT WE CLAIM IS:—

1. A process of increasing the silica/alumina ratio in the crystal lattice of a crystalline zeolitic aluminosilicate which comprises exposing the aluminosilicate, while at least partially in the hydrogen form, to hydrolysis to such extent that at least 50% of the crystallinity of the aluminosilicate is retained, treating said aluminosilicate with a complexing agent to form a coordination complex with the aluminium which has been displaced from the crystal lattice, and separating at least part of the said coordination complex from the aluminosilicate.

2. A process as defined in claim 1 wherein said complexing agent is a chelating agent which will form a stable chelate with said aluminium.

3. A process as defined in claim 2 wherein said chelating agent forms a soluble chelate with aluminium in the medium in which said chelation is effected, said aluminosilicate being insoluble in said medium both before and after chelation.

4. A process as defined in claim 2 or claim 3 wherein said chelating agent forms a chelate with at least one cation in said aluminosilicate which chelate is soluble in the medium in which said chelation is effected.

5. A process as defined in any one of claims 2 to 4 wherein said chelating agent is also effective to convert said aluminosilicate at least partially to its hydrogen form prior to the hydrolysis step.

6. A process as defined in any one of claims 2 to 5 said chelating agent is selected from the group consisting of ethylenediaminetetraacetic acid, carboxylic acids, polycarboxylic acids, acid salts of said acids, and mixtures thereof.

7. A process as defined in any one of claims 2 to 5 wherein said chelating agent is di (tetraethylammonium) dihydrogen ethylenediaminetetraacetic acid.

8. A process as defined in any one of claims 1 to 7 wherein said aluminosilicate is in the faujasite form before the hydrolysis step.

9. A process as defined in any one of claims 1 to 7 said aluminosilicate is in the Y form before the hydrolysis step.

10. A process as defined in claim 9 wherein

said aluminosilicate is in the calcium Y form before the hydrolysis step.

11. A process as defined in claim 5 wherein said chelating agent is only weakly acid and wherein said aluminosilicate contains cations prior to the hydrolysis step which form sufficiently stable chelates with said chelating agent to provide the reaction potential to cause hydrogen ions in the chelating agent to exchange into cation sites in said aluminosilicate.

12. A process as defined in claim 2 wherein said chelating agent forms a stable chelate with said aluminum which is insoluble in the medium in which the chelation is effected.

13. A process as defined in claim 12 wherein said chelating agent is an anion exchange resin which will form a stable chelate with aluminum and which, after chelation of said aluminosilicate, will be of a size sufficiently different from that of the alumina-deficient aluminosilicate to be separated therefrom by a classification technique.

14. A process as defined in claim 2 wherein said chelating agent forms a stable chelate with at least one cation in said aluminosilicate.

15. A process as defined in any one of claims 1 to 14 wherein the pH of the hydrolysis reaction mixture is below 7 at at least some point during the hydrolysis.

16. A process as defined in any one of claims 2 to 15 the pH of said chelating agent is no greater than 6.

17. A method according to any one of claims 1 to 16 wherein said aluminosilicate is converted at least partially to the hydrogen form and then hydrolyzed.

18. A method as defined in any one of claims 1 to 17 wherein the silica/alumina ratio in the initial aluminosilicate is at least 2/1.

19. A method as defined in any one of claims 1 to 18 the silica/alumina ratio in the initial aluminosilicate is at least 4/1.

20. A method as defined in any one of claims 1 to 18 wherein the silica/alumina ratio in the initial aluminosilicate is between 2/1 and 6/1.

21. A method according to any one of claims 1 to 20 wherein said aluminosilicate is treated with a fluid medium containing a chelating agent which forms stable chelates with aluminum.

22. A method as defined in claim 21 wherein said chelating agent also forms stable chelates with at least one cation which is present in said aluminosilicate.

23. A method as defined in claim 22 wherein said chelating agent is effective to convert said aluminosilicate into the acid form during the chelating operation.

24. A method as defined in claim 23 wherein said aluminosilicate is hydrolyzed after being

converted to its acid form by said chelating agent no later than said chelating operation.

25. A method as defined in claim 24 wherein said chelating agent contains at least one cation other than hydrogen and wherein said cation is too large to be exchanged into said aluminosilicate to any substantial extent.

26. A process according to any one of claims 1 to 25 for altering the properties of a crystalline aluminosilicate with a change in chemical composition of the ordered anionic structure while substantially retaining crystallographic character as indicated by X-ray diffraction pattern wherein said aluminosilicate is sufficiently treated with a fluid medium containing a chelating agent for aluminum ions to remove aluminum from the crystal lattice of said aluminosilicate, leaving a crystal structure which appears by X-ray diffraction to contain silicon atoms which are not actually present.

27. A method according to any one of claims 1 to 26 wherein said aluminosilicate is treated with a complexing agent which will form coordination complexes with aluminum ions, the pH of the reaction mixture including said aluminosilicate and said complexing agent being below 7 at at least some point during the treatment.

28. A method of increasing the silica/alumina ratio of a crystalline aluminosilicate substantially as described herein with reference to the Examples.

29. Crystalline aluminosilicates, whenever prepared by the method of any one of claims 1 to 28.

30. A method for transforming an organic compound which is catalytically convertible in the presence of acidic catalyst sites comprising contacting said organic compound under conversion conditions with an aluminosilicate according to claim 29.

31. A method for transforming an organic compound, catalytically convertible in the presence of acidic catalyst sites, which comprises placing said organic compound, under conversion conditions, in the presence of a catalyst composition selected from the group consisting of porous crystalline aluminosilicates characterized by a hydrocarbon adsorption capacity greater than would be theoretically calculated from a combined X-ray diffraction and elemental chemical analysis of said catalyst composition.

32. Organic compounds when formed by the method of claim 30 or claim 31.

For the Applicants,
CARPMAELS & RANSFORD,
Chartered Patent Agents,

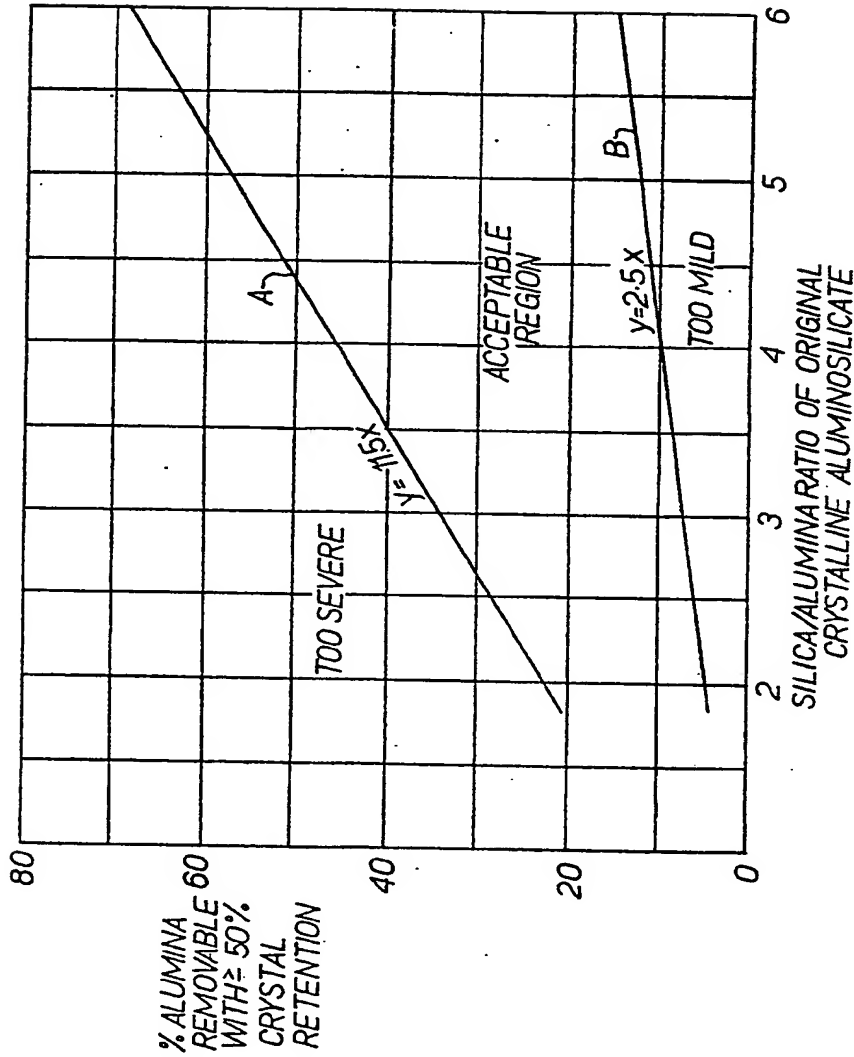
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